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Alternatives to Calcium-based SO2 Sorbents for Fluidized-Bed Combustion Conceptual Evaluation

Westinghouse Research and Development Center, Pittsburgh, Pa

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ALTERNATIVES TO CALCIUM-BASED SO_2 SORBENTS FOR FLUIDIZED-BED COMBUSTION: CONCEPTUAL EVALUATION

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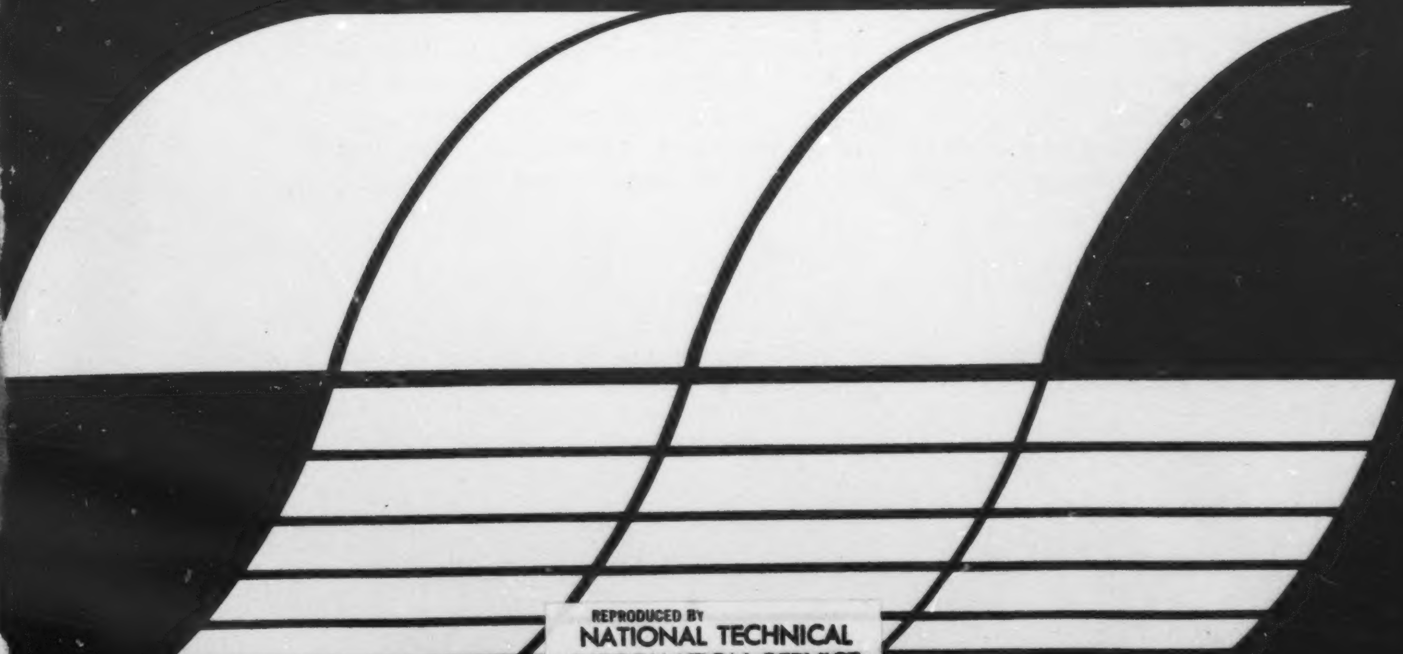

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16. ABSTRACT The report gives results of a conceptual engineering evaluation to screen supported metal oxides as alternatives to natural calcium-based sorbents (limestones and dolomites) for SO2 control in atmospheric and pressurized fluidized-bed combustion (FBC) processes. Alternative sorbents were evaluated, using three acceptance criteria: SO2 removal capability in the combustor, predicted by thermodynamics; SO2 concentrations achievable in the regenerator off-gas, according to thermodynamics; and SO2 concentrations off the regenerator, achievable based on material and energy balances. The evaluation identified 14 potentially acceptable sorbents for atmospheric FBC, and 11 for pressurized FBC. Cost estimates were prepared to project the maximum acceptable loss rates for the alternative sorbents due to attrition and/or deactivation. Loss rates must be less than 0.1% of bed inventory per hour in order to compete economically with natural calcium-based sorbents, even if maximum thermodynamic performance were obtained. U.S. resources of some minerals may be of extreme importance for many of the alternative metal oxide sorbents considered.

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Fluidized-bed Processing	Limestone	Stationary Sources	08G
Combustion	Dolomite (Mineral)	SO2 Sorbents	13H,07A
Sulfur Dioxide		Metal Oxides	21B
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ALTERNATIVES TO CALCIUM-BASED SO_2 SORBENTS FOR FLUIDIZED-BED COMBUSTION: CONCEPTUAL EVALUATION

by

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PREFACE

The Westinghouse R&D Center is carrying out a program to provide experimental and engineering support for the development of fluidized-bed combustion systems under contract to the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency (EPA), at Research Triangle Park, NC. The contract scope includes atmospheric and pressurized fluidized-bed combustion processes as they may be applied for steam generation, electric power generation, or process heat. Specific tasks include work on calcium-based sulfur removal system studies (e.g. sorption kinetics, regeneration, attrition, modeling), alternative sulfur sorbents, nitrogen oxide emissions, particulate emissions and control, trace element emissions and control, spent sorbent and ash disposal and systems evaluation (e.g. impact of new source performance standards on fluidized-bed combustion system design and cost.

This document contains the results of work, defined and completed under the alternative sorbent task, from December 1975 to December 1976. Results from work carried out by Westinghouse or reported by other

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*Experimental work at Exxon (L.A. Ruth, "Regenerable Sorbents for Fluidized-Bed Combustion," Proceedings of the Fluidized-Bed Combustion Technology Exchange Workshop, Vol. II, 301, NTIS No. CONF-770447-P-2, April 1977), and Argonne National Laboratory (R.B. Snyder et al, Synthetic Sorbents for Removal of Sulfur Dioxide in Fluidized-Bed Combustors", June 1977, NTIS No. ANL/CEN/FE-77-1) has been reported since this evaluation. Their results complement this report by extending the experimental base for the evaluation.

investigators after February 1977 are not integrated into this task report.* The work reported represents an extension of prior work completed by Westinghouse under contract to EPA. Results from this prior work on fluidized-bed combustion include:

- Assimilation of available data on fluidized-bed combustion, including sulfur dioxide removal, sorbent regeneration, sorbent attrition, nitrogen oxide minimization, combustion efficiency, heat transfer, particle carry-over, boiler tube corrosion/erosion fouling, and gas-turbine erosion/corrosion deposition
- Assessment of markets for industrial boilers and utility power systems
- Development of designs for fluidized-bed industrial boilers
- Development of designs for fluidized-bed combustion utility power systems: atmospheric-pressure fluidized-bed combustion boiler combined-cycle power systems, adiabatic fluidized-bed combustion combined-cycle power systems--including first- and second-generation concepts
- Preparation of a preliminary design and cost estimate for a 30 MW (equivalent) pressurized fluidized-bed combustion boiler development plant
- Assessment of the sensitivity of operating and design parameters selected for the base power plant design on plant economics
- Collection of experimental data on sulfur removal and sorbent regeneration using limestone and dolomites
- Preparation of cost and performance estimates for once-through and regenerative sulfur removal systems
- Evaluation of alternative sulfur sorbents
- Collection and analysis of data on spent sorbent disposal--utilization and environmental impact of disposal

- Projection and analysis of trace emissions from fluidized-bed combustion systems
- Analysis of particulate removal requirements and development of a particulate control system for high-temperature, high-pressure fluidized-bed combustion systems
- Construction of a high-pressure/temperature particulate control test facility
- Development of plant operation and control procedures
- Construction of a corrosion/erosion test facility for the 0.63 MW Exxon miniplant
- Continued assessment of fluidized-bed combustion power plant cycles and component designs to evaluate environmental impact.

The results of these surveys, designs, evaluations, and experimental programs provide the basis for the work being carried out under the current contract. Seven reports are available that document the prior contract work (see references 16-18).

ABSTRACT

A conceptual engineering evaluation has been performed to screen supported metal oxides as alternatives to natural calcium-based sorbents (limestones and dolomites) for SO_2 control in fluidized-bed combustion processes. Ranges of applicable operating conditions for atmospheric-pressure fluidized-bed combustion (AFBC) and for pressurized fluidized-bed combustion (PFBC) have been defined. Acceptance criteria for thermodynamic performance, melting point, and material-and-energy balance limitations of metal oxides in the combustor and in the sorbent regeneration process have been proposed and applied in the evaluation.

Three regenerative schemes for the alternative sorbents have been considered, and ranges of operating conditions resulting in acceptable performance for the sorbents have been identified. Fourteen potentially acceptable sorbents have been identified for AFBC and eleven for PFBC.

Estimates of regeneration system economics, sorbent cost (supported on alumina), and sorbent availability have been developed in order to project maximum acceptable loss rates for the sorbents.

Sorbent loss rates, due to attrition or deactivation, must be small relative to calcium-based sorbents (less than 0.1 percent of bed content per hour) in order to compete economically with natural calcium-based sorbents, even if maximum thermodynamic performance is realized. Sorbent availability will be of extreme importance for many metal oxide materials. Recommendations are made for further engineering assessment and experimental sorbent screening.

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SECTION 1

INTRODUCTION

Conventional steam-turbine cycles and combined steam- and gas-turbine cycles are bring utilized with fluidized-bed coal combustion techniques, (e.g., atmospheric-pressure fluidized-bed boilers, supercharged fluidized-bed boilers, and adiabatic combustors) to develop power generation systems having superior environmental control and economics. Current development programs primarily emphasize the use of calcium-based sorbents (limestones and dolomites) to provide in situ control of SO_x in the combustor.

First-generation fluidized-bed combustion power plants will operate with once-through utilization of the calcium-based sorbents to generate calcium sulfate containing, dry, granular, spent sorbent material. The quantity of spent sorbent produced will be approximately one to four times as much as is produced by an equivalent limestone wet scrubber (on a dry basis) for a conventional power plant but will be easier to handle and may be environmentally more acceptable than the sludge produced by wet scrubbing.

For second-generation fluidized-bed combustion power plants regeneration processes using calcium-based sorbents are being studied for the purpose of reducing the quantity and environmental impact of spent sorbent material. The state of development of regeneration processes for calcium-based sorbents is characterized by bench-scale experimentation and uncertain performance and economic feasibility.

An alternative to limiting calcium-based spent sorbent production by sorbent regeneration is utilizing other granular sorbent material in the place of calcium-based sorbents. Alternative sorbents are expected to be much more expensive than natural calcium-based sorbents in the place of calcium-based sorbents. Alternative sorbents are expected to be much more expensive than natural calcium-based sorbents because of raw material preparation. In order to be successful they must be highly regenerable and free from loss in physical integrity. The sorbent must result in acceptable plant performance and economics.

This report on alternative sulfur removal sorbents presents the results of the work scheduled to identify alternative sorbents, for atmospheric and pressurized fluidized-bed combustion systems, to evaluate their technical and economic potential, and to identify development requirements. Recommendations for experimental and alternative sorbent system development work are presented.

In this report potentially attractive alternative sorbents for fluidized-bed combustion (simple metal oxides and mixed metal oxides) are identified by screening evaluations of performance and economic factors. Performance criteria are developed for utilization in experimental data evaluation.

In conducting this screening, thermodynamic, melting point, and material and energy balance limitations for simple and double metal oxides have been projected. Estimates of sorbent availability and economic limitations are developed and translated into maximum tolerable rates of alternative sorbent losses from all causes (attrition, elutriation deactivation, agglomeration, etc.). Optimistic assumptions are applied in the screening evaluation in order to project maximum sorbent potential. Critical design and testing areas are identified and a program plan is developed to evaluate attractive alternative sorbents in more detail (Appendix A).

An alternative once-through calcium-based sorbent concept for fluidized-bed combustion has also been evaluated (Appendix B). The concept, "Intimate Coal/Sorbent Mixtures," applies methods of bringing coal and calcium oxide into intimate contact during coal combustion to improve calcium utilization and SO_x emission control, and to reduce the quantity of spent sorbent. Techniques for realizing intimate contact are screened and the most promising technique,pelletization of coal and sorbent into consolidated particles, is evaluated with respect to performance potential and economic limitations.

SECTION 2

CONCLUSIONS

ALTERNATIVE SORBENTS

- Fourteen alternative sorbents have been identified as possibly suitable for atmospheric pressure fluidized-bed combustion: Na_2CO_3, $CaO/CaCO_3$, $SrCO_3$, $BaCO_3$, $LiAlO_2$, $LiFeO_2$, Li_2TiO_3, $NaAlO_2$, $NaCO_3 \cdot Fe_2O_3$, $CaAl_2O_4$, $SrAl_2O_4$, $SrTiO_4$, $BaAl_2O_4$ and $BaTiO_3$.
- Eleven sorbents are possibly suitable for pressurized fluidized-bed combustion: $CaO/CaCO_3$, Sr_2CO_3, $BaCO_3$, $LiAlO_2$, $LiFeO_2$, Li_2TiO_3, $CaAl_2O_4$, $SrAl_2O_4$, $SrTiO_3$, $BaAl_2O_4$ and $BaTiO_3$.
- The availability of the active sorbent material or the support material will be a very important factor in justifying the development of fluidized-bed combustion with alternative sorbents.
- If maximum sorption/regeneration performance levels could be achieved, it is expected that alternative sorbent loss rates (due to attrition, deactivation, etc.) must be less than 0.1 percent of bed content per hour in order to compete economically with regenerative limestone/dolomite-based fluidized-bed combustion (reductive decomposition regeneration). This criterion must be translated into experimental performance goals for cyclic-kinetic studies and attrition studies.
- Attrition behavior under simulated process conditions should be characterized in order to select promising support materials, although availability may determine the support material.

- The kinetics of desulfurization and regeneration should be characterized within the applicable range of operating conditions (temperature, pressure, fuel, etc.) and under conditions which simulate the maximum performance levels.
- Unless the high levels (near maximum) of SO_2 or H_2S projected in this report can be achieved in the regeneration process, the alternative sorbents will be economically unfeasible.
- At present, too little is known about the cost of sorbent preparation. Feasible process technology for sorbent preparation should be proposed and the economic feasibility assessed.
- The availability of the sorbent materials and the support materials require more modeling in order properly to assess all of the market factors. The area of industrial expansion into alternative sorbent preparation and distribution must also be explored.
- Alternative sorbents may require alternative fluidized-bed combustion design concepts to satisfy their limitations and promote their advantages. The impact of alternative designs that would reduce sorbent attrition/deactivation should be evaluated (e.g., low fluidization velocities, fine particles, shallow beds, low thermal shock control).
- The environmental impact of alternative sorbents may lead to elimination of certain candidate materials (spent sorbent disposal, trace metals release, impact on NO_x, CO, particulates, etc.). The complex sociological interactions of these materials must be explored before development is committed.

INTIMATE COAL/SORBENT MIXTURES

- The only intimate coal/sorbent mixture that could be identified as being technically feasible for the current fluidized-bed combustion design concept is the pelletization of coal and sorbent into consolidated particles.

- Attrition of the consolidated particle is the critical factor influencing the performance and feasibility of the concept. Modifications to the combustor design would probably be required in order to apply the consolidated particle concept.
- The performance (technical and environmental) cannot be estimated without initiating a test program. The overall technical and environmental performance of the consolidated particle concept could conceivably be worse than or greater than the case of conventional coal and sorbent injection into a fluid-bed combustor, but it is probable that no significant improvement in performance will be realized.
- Except under very extreme conditions, the consolidated particle concept will not be economically competitive with conventional fluid-bed combustion concepts.
- Washing the pulverized coal during consolidated particle preparation could reduce trace elements, ash, sulfur, and the sorbent requirement. The economics of this option have not been investigated.
- The most attractive consolidated coal/sorbent particle from a technical and environmental impact standpoint would utilize a binder that would maintain the coal-ash and sorbent particles in discrete, consolidated particles following combustion. A binder that will provide this behavior has not yet been identified.

SECTION 3

RECOMMENDATIONS

ALTERNATIVE SORBENTS

- The three most promising alternative sorbents, $BaCO_3$, $CaAl_2O_4$, and $BaTiO_3$, are recommended for further evaluation.
- The following tasks are recommended for the next phase of the current program to be performed with the selected sorbents:
  1. Further evaluation of the availability, cost, and properties of selected sorbents and support materials through contacts with industrial suppliers
  2. Evaluation of alternative sorbent commercial preparation methods and preparation costs
  3. Preparation of the selected sorbents, using commercial preparation techniques, and evaluation of the prepared sorbents' physical and chemical properties
  4. Collection of data on desulfurization kinetics and regeneration kinetics on small-scale TGA and fluid-bed units under high-performance conditions. Tests on sorbent attrition at process conditions.
  5. Assessment of plant performance and cost with the selected sorbents
  6. Proposal of development plan for the best alternative sorbent if, based on the above evaluation, one appears commercially advantageous compared to the naturally occurring calcium-based sorbent materials.
- On the basis of availability considerations, the support material should be alumina. The prepared alumina properties to be

utilized must provide a trade-off between low cost, high attrition resistance, high sorbent kinetics promoted by large pore diameters, and the amount of active sorbent that can be loaded. Alumina suppliers should be contacted.

INTIMATE COAL/SORBENT MIXTURES

- The concept of intimate coal/sorbent mixtures should not be pursued unless a binder can be identified that will maintain the structure of the consolidated coal/sorbent particles following combustion, or unless the economics of washing the pulverized coal to remove sulfur and ash during consolidated particle preparation is found to be attractive
- The areas of improved binder identification and pulverized coal-washing evaluation are recommended for further study by engineering assessment or small-scale experimentation.

SECTION 4

SCOPE AND METHOD OF ASSESSMENT

The possibility that there are alternative sorbents for SO_2 absorption that are superior to naturally occurring calcium-based sorbents (limestones and dolomites) in terms of performance and economics has been the subject of several previous screening studies.[7] Two of the studies have specifically considered the application of regenerative alternative sorbents to atmospheric-pressure fluidized-bed combustion.[6,7] These studies, in general, are devoted to the discussion of the thermodynamic potential, with additional but limited comment on sorbent cost and availability.

In the present screening evaluation of alternative sorbents for fluidized-bed combustion, both atmospheric-pressure and pressurized combustion systems are considered. Operating conditions applicable to the combustion systems and sorbent regeneration systems are defined, and acceptance criteria used to judge thermodynamic, material, and energy balance limitations are developed and specified. Alternative sorbents satisfying these criteria are evaluated by simple models for availability and cost limitations in order to project maximum acceptable rates of sorbent loss due to attrition, elutriation, deactivation, agglomeration, and the like. The results provide a qualitative perspective, rather than quantitative design factors, on the required sorbent behavior.

The purpose of the study is to identify acceptable alternative sorbents for fluidized-bed combustion and to recommend testing areas that will further assess their potential. Critical process evaluations are also recommended.

On the basis of screening results, an experimental testing program has been devised to evaluate the critical performance factors of selected alternative sorbents (Appendix IIIA). Specific test conditions and acceptance criteria for the tests are proposed.

In addition, a second fluidized-bed combustion process concept is evaluated (Appendix IIIB). This concept is based on "intimate coal/sorbent mixtures" and is an alternative once-through sorbent concept for calcium-based sorbents.

SYSTEM CONCEPTS

The general concept applied is analogous to the current fluidized-bed combustion concepts based on calcium-based sorbents (limestone or dolomite): in situ coal combustion and in situ desulfurization within a fluidized-bed environment using granular sorbent as the bed material. Three variations of the fluidized-bed combustion process are represented: The atmospheric-pressure fluidized-bed boiler (AFBC), the pressurized fluid-bed boiler with combined-cycle power generation, and the adiabatic fluidized-bed combustor, also based on combined-cycle operation (PFBC). In addition, each of these concepts may utilize either current or advanced turbine technology, leading to changes in the applicable operating conditions of the fluidized-bed combustor.

Four concepts for the regeneration of the sorbent are evaluated:

1. Thermal decomposition:

$$\mathrm{MeSO_4} \rightleftharpoons \mathrm{MeO} + \mathrm{SO_2} + 1/2\ \mathrm{O_2}$$

where MeO represents a metal oxide and $\mathrm{MeSO_4}$ is a metal sulfate.

2. Reductive decomposition:

$$\mathrm{MeSO_4} + \left\{\begin{matrix}\mathrm{H_2} \\ \mathrm{CO}\end{matrix}\right\} \rightleftharpoons \mathrm{MeO} + \mathrm{SO_2} + \left\{\begin{matrix}\mathrm{H_2O} \\ \mathrm{CO_2}\end{matrix}\right\} .$$

3. A two-step process based on sulfate reduction to sulfide followed by H_2S generation by steam reaction:

$$MeSO_4 + 4\begin{Bmatrix}H_2\\CO\end{Bmatrix} \rightleftharpoons MeS + 4\begin{Bmatrix}H_2O\\CO_2\end{Bmatrix}$$

$$MeS + H_2O \rightleftharpoons MeO + H_2S$$

where MeS is a metal sulfide.

4. Finally, a two-step process in which the H_2S generation step is based on steam/carbon dioxide reaction:

$$MeSO_4 + 4\begin{Bmatrix}H_2\\CO\end{Bmatrix} \rightleftharpoons MeS + 4\begin{Bmatrix}H_2O\\CO_2\end{Bmatrix}$$

$$MeS + CO_2 + H_2O \rightleftharpoons MeCO_3 + H_2S$$

where $MeCO_3$ is a metal carbonate.

It is assumed that all energy and reductant requirements for regeneration are supplied by coal utilization rather than by clean fuels.

The concept of a once-through operation with an alternative sorbent is rejected on the grounds that no commercially manufactured alternative sorbent could compete economically with a limestone or dolomite in once-through operation. No inexpensive, naturally occurring alternative sorbents can be identified whose performance can compete with that of limestone and dolomite. Thus, the use of alternative sorbents must be based on the concept of preparing an artificial sorbent by chemical processing from the raw sorbent constituents and a suitably prepared support material,and must be characterized by improved regenerability and reduced attrition and deactivation relative to naturally occurring calcium-based sorbents.

OPERATING CONDITIONS AND ACCEPTANCE CRITERIA

The operating conditions selected for the three fluidized-bed combustion concepts are based on the conditions required for optimum power generation. Table 1 lists the ranges of conditions for the fluidized-bed combustion systems with current and advanced turbine technology. Fluidized-bed combustor pressure, the normal operating temperature range, turndown temperature, and the excess air levels in the combustor are listed. It is assumed that the combustor temperature should not exceed the agglomeration temperature of the coal (selected as 1040°C) or the sorbent melting point. The resulting flue gas composition (percent oxygen, carbon dioxide, and SO_x emission required to meet the EPA emission standard for coal-fired power plants) is also presented. The equilibrium SO_x level (SO_2 plus SO_3) of which the alternative sorbent must be capable at combustion conditions is selected as 20 percent of the emission standard value in order to provide a reasonable reaction driving force in the combustor. The selection of this criterion is rather arbitrary, but the general results do not depend critically upon it.

The regeneration system operating conditions must be compatible with the combustor operating conditions. The conditions are listed in Table 2,for each of the power cycle concepts with regeneration,by thermal decomposition, reductive decomposition, or the two-step processes. Again, the regenerator temperature should not exceed the agglomeration point of the bed or the melting point of the sorbent, taken here as 1400°C to account for the possibility of high softening-point coals. The minimum equilibrium value of SO_2 (4 mole %) or H_2S (3 mole %) generated in the regenerator is listed,based on a knowledge of the requirements for sulfur recovery processes.

Material and energy balance constraints will be limiting in many cases of high equilibrium potential (e.g., the energy required for the reaction system may require the addition of energy combustion of coal such that the combustion products dilute the reaction products to levels below equilibrium values).

TABLE 1. FLUIDIZED-BED COMBUSTOR CONDITIONS AND CRITERIA

System	Bed Pressure, kPa (atm)	Bed Temperature		Flue Gas Composition				Equilibrium Criteria for SO_x[d] ppm
		Normal °C	Minimum[a] °C	Excess Air[b] %	O_2, %	CO_2, %	SO_x Emission ppm[c]	
Atmospheric Boiler (AFBC)								
Current turbine technology(e)	100 (1)	650–1040	600	10–25	2–4	15–13	600–530	120–106
Advanced turbine technology[f]	100 (1)	760–1040	700					
Pressurized Boiler (PFBC)								
Current turbine technology	1000 (10)	900–1040	760	10–100	2–10	15–8.5	600–330	120–66[h]
Advanced turbine technology[g]	1000 (10)	900–1040	760					
Adiabatic Combustor (PFBC)								
Current turbine technology	1000 (10)	900–1040	760	300	16	4.25	166	33

[a] Estimated minimum bed temperature during turndown.

[b] Based on complete combustion of the fuel carbon and hydrogen to CO_2 and H_2O; neglects O_2 and N_2 in the coal and combustion of the fuel sulfur.

[c] Based on current EPA SO_2 emission standard of 0.516 kg SO_2/GJ.

[d] Based on equilibrium SO_x (SO_2 + SO_3) equal to 20% of SO_2 standard to provide reasonable kinetic driving force in the desulfurizer.

[e] Current steam-turbine technology 540°C (1000°F) steam superheat temperature.

[f] Advanced steam-turbine technology 650°C (1200°F) steam superheat temperature.

[g] Refers only to steam-turbine technology; although advanced gas-turbine inlet conditions of up to 1540°C (2800°F) and 250 kPa (25 atm) are forecast, the maximum bed operating temperature of 1040°C (1900°F) (based on ash softening) restricts gas turbines to current technology of 870–1040°C (1600–1900°F) and 800–1000 kPa (8–10 atm). Coals having higher ash-softening points or alternative fuels (residual fuel oils, etc.) could conceivably utilize advanced gas-turbine technology but are not considered.

[h] Alternatively, a level of about 10 ppm could greatly improve turbine corrosion performance, and sorbents having this capability should be so noted.

TABLE 2. REGENERATION CONDITIONS AND CRITERIA

Combustion System	Bed Pressure,[a] kPa (atm)	Bed Temperature[b]	Fuel Type[c]	Reducing Gas System[d]	Equilibrium SO_2 or H_2S Criteria[e] (mole %)	Energy and Material Balance Maximum SO_2[f] (mole %)
Atmospheric Boiler (AFBC)						
Thermal decomposition	100 (1)	Less than coal agglomeration (~1400°C) or sorbent melting point	Coal	—	>4	>4
Reductive decomposition	100 (1)		Coal	in situ	>4	>4
Two-step	100 (1)		Coal			
1st step				in situ	$<10^{-2}$ [g]	—
2nd step				—	>3 (H_2S)	>3
Pressurized Boiler or Adiabatic Combustor (PFBC)						
Thermal decomposition	1000 (10)	Less than coal agglomeration (~1400°C) or sorbent melting point	Coal	—	>4	>4
Reductive decomposition	1000 (10)		Coal	in situ	>4	>4
Two-step	1000 (10)		Coal			
1st step				in situ	$<10^{-2}$ [g]	—
2nd step				—	>3 (H_2S)	>3

---

[a] Bed pressure should be close to the combustor pressure based on sorbent circulation feasibility; some difference can be tolerated - expected to be about 100 kPa difference for the atmospheric boiler case and up to 500 kPa for the pressurized cases.

[b] The maximum regeneration temperature may be based upon bed sintering (agglomeration), sorbent deactivation, energy restrictions, economics, etc.

[c] Coal will be used to supply energy in all cases except where the amounts required are trivial.

[d] If reducing gas is generated by in situ coal partial combustion, then the ash agglomeration point may limit the operating temperature or an agglomerating bed with ash-sorbent separation may be used.

[e] Lower SO_2 or H_2S concentrations require large equipment, energy requirements, and difficult sulfur recovery. In practical terms sorbents providing SO_2 greater than 10 mole % will be more realistic. The generation of MeS can be tolerated as long as the SO_2 content meets the specified criteria and the sorbent circulation rate does not reach unreasonably high rates.

[f] The maximum SO_2 concentration based on stoichiometry and energy balance assumptions may be estimated and is related to the rate of MeS generation. In practical terms, 10 mole % SO_2 is more realistic.

[g] H_2S and other sulfur products generated in the first step may be released if they meet environmental requirements or may be recycled to the combustor if necessary.

Minimum values of SO_2 or H_2S based on material and energy balances are also selected at 4 and 3 mole % for SO_2 and H_2S, respectively. The extent of sorbent regeneration (fraction of sulfate converted to oxide) is a process variable which is not directly restricted. Any value is acceptable if it leads to acceptable sorbent activity and system economics.

The rate of sorbent losses due to attrition or deactivation is not constrained by thermodynamics or material and energy balance considerations but by sorbent availability and cost considerations. Sorbent losses are evaluated parametrically later in this report to provide guidance for sorbent attrition testing.

Of course, in a practical system design many other sorbent characteristics will be of great importance. The kinetics of desulfurization and regeneration are obviously important and depend upon such factors as the structure of the sorbent and the operating conditions. Such factors as environmental impact (e.g., trace element release in the combustor and leaching properties of the spent sorbent), particle agglomeration, fluidization quality, bed mixing behavior, heat transfer, tube erosion and corrosion, bed pressure drop, turbine protection, and safety must eventually be addressed to find the attractive alternative sorbents.

In summary, the initial sorbent screening is based upon the following acceptance criteria:

- Thermodynamically predicted SO_2 control capabilities in the combustor
- Thermodynamically predicted SO_2 or H_2S concentrations achievable from the regenerator
- SO_2 or H_2S concentrations from the regenerator based on material and energy balances
- Phase-change limits (melting), based on sorbent physical properties, relative to the acceptable combustor and regenerator operating conditions.

The approach is to eliminate any sorbent from consideration once it is determined that it does not meet any one of the acceptance criteria. This method of elimination quickly reduces the number of candidates and reduces to a minimum the effort required at each stage of the study. Optimistic assumptions are applied in order to determine the maximum possible sorbent performance.

The assessment based upon each of the acceptance criteria is discussed in Sections 5, 6, and 7 of this report. The sorbents which meet all four of the criteria are then evaluated further in Sections 8 and 9 on the basis of availability and economics.

SORBENT MATERIALS CONSIDERED

Only metal oxides have been previously identified as potential SO_2 sorbents. Both simple metal oxides and double oxides are evaluated. The initial list of sorbents to be considered and those not to be evaluated are selected from previous studies[5-7] and are listed in Tables 3 and 4. The explanations provided in the original studies for the sorbents not considered are also included in Table 4 and were accepted without further assessment.

Alternative support materials for the sorbent structure are discussed under the topic of availability since it is assumed they do not affect the sorbent thermodynamic behavior. While interactions between the sorbent material and support material may occur, this assumption is reasonable for the initial screening.

TABLE 3. INITIAL LIST OF ALTERNATIVE SORBENTS EVALUATED (METAL OXIDES)

Li_2O	Al_2O_3	$KAlO_2$	$SrAl_2O_4$
Na_2O	SnO_2	K_2CrO_4	$SrCrO_4$
K_2O	PbO	$K_2Cr_2O_4$	$SrCr_2O_4$
BeO	Sb_2O_3	$KFeO_2$	$SrFe_2O_4$
MgO	Bi_2O	K_2TiO_3	$SrTiO_3$
CaO	UO_3	KVO_3	SrV_2O_6
SrO	ThO_2		
BaO		$BeAl_2O_4$	$BaAl_2O_4$
La_2O_3	$LiAlO_2$	$BeCrO_4$	$BaCrO_4$
Ce_2O_3	Li_2CrO_4	$BeCr_2O_4$	$BaCr_2O_4$
CeO_2	$Li_2Cr_2O_4$	$BeFe_2O_4$	$BaFe_2O_4$
ZrO_2	$LiFeO_2$	$BeTiO_3$	$BaTiO_3$
V_2O_4	Li_2TiO_3	BeV_2O_6	BaV_2O_6
Mn_2O_3	$LiVO_3$		
Fe_2O_3		$CaAl_2O_4$	
CoO	$NaAlO_2$	$CaCrO_4$	
NiO	Na_2CrO_4	$CaCr_2O_4$	
CuO	$Na_2Cr_2O_4$	$CaFe_2O_4$	
Ag_2O	$NaFeO_2$	CaV_2O_6	
ZnO	Na_2TiO_3		
CdO	$NaVO_3$		

TABLE 4. METAL OXIDES NOT CONSIDERED BECAUSE OF PREVIOUS JUDGMENTS

Sorbent	Explanation	Sorbent	Explanation
Rb_2O	3	MnO	1
Cs_2O	3	MnO_2	1
Sc_2O_3	2	ReO_2	2
Y_2O_3	2	FeO	1
TiO_2	2	IrO_2	2
HfO_2	2	PdO	2
V_2O_3	1	Cu_2O	1,3
VO_2	1	Ga_2O_3	2
Nb_2O_5	2	SiO_2	4
Ta_2O_5	2	GeO_2	2
Cr_2O_3	4	As_2O_3	2
MoO_3	3	Double oxide silicates	2
WO_3	2	$CaTiO_3$	2

1 - Not stable oxide form at combustor conditions.
2 - Insufficient data.
3 - Low melting point.
4 - Other.

SECTION 5

PROJECTIONS OF DESULFURIZATION PERFORMANCE

Alternative sorbents having acceptable desulfurization potential are identified by examining three areas:

- The equilibrium behavior of the desulfurization reaction $MeO + SO_2 + 1/2\ O_2 \leftrightarrows MeSO_4$
- The melting points characteristic of the sorbent materials
- The metal carbonate stability $MeO + CO_2 \rightleftarrows MeCO_3$ in the desulfurizer environment.

EQUILIBRIUM DESULFURIZATION PERFORMANCE

Data are available on the equilibrium behavior of the reactions$^{5-7}$

$$MeSO_4 \rightleftarrows MeO + SO_3,\ K_1 = X_{SO_3} P$$

$$SO_3 \rightleftarrows SO_2 + 1/2\ O_2,\ K_2 = \frac{X_{O_2}^{1/2} X_{SO_2}}{X_{SO_3}} P$$

where X_i is the mole fraction of species i and K is the appropriate equilibrium constant.

The total SO_x concentration at equilibrium is

$$X_{SO_x} = X_{SO_2} + X_{SO_3} = \frac{K_1}{P} + \frac{K_1 K_2}{X_{O_2}^{1/2} P^{3/2}} \ .$$

The limiting values for K_1 can be determined for each fluidized-bed combustion variation based upon the pressures, temperatures and oxygen concentrations given in Table 1; the equilibrium criteria SO_2 concentration given in the last column of Table 1; and the value of K_2 obtained from the literature. Table 5 presents values for the limit curves for sorbent acceptance.

Curves giving the equilibrium constant for 32 metal oxides are shown in Figures 1 and 2 (see curves 1 through 32), together with the limit curves for $\log_{10} K_1$ taken from Table 5 (see curves A through D). The potentially acceptable sorbents and their maximum operable combustor temperatures have been determined on the basis of Figures 1 and 2. Results are shown in Table 6. Note that the number of potential sorbents for the pressurized systems is much lower than that for the atmospheric pressure boiler. The 29 sorbents included in Table 3 but not listed in Table 6 are entirely below the limit curves and are thus eliminated from further consideration. In addition, curves are not shown for Li_2O, Na_2O, K_2O, CaO, SrO, BaO, $LiAlO_2$ and Li_2TiO_3, all of which lie far above the limit curves and are,thus, acceptable.

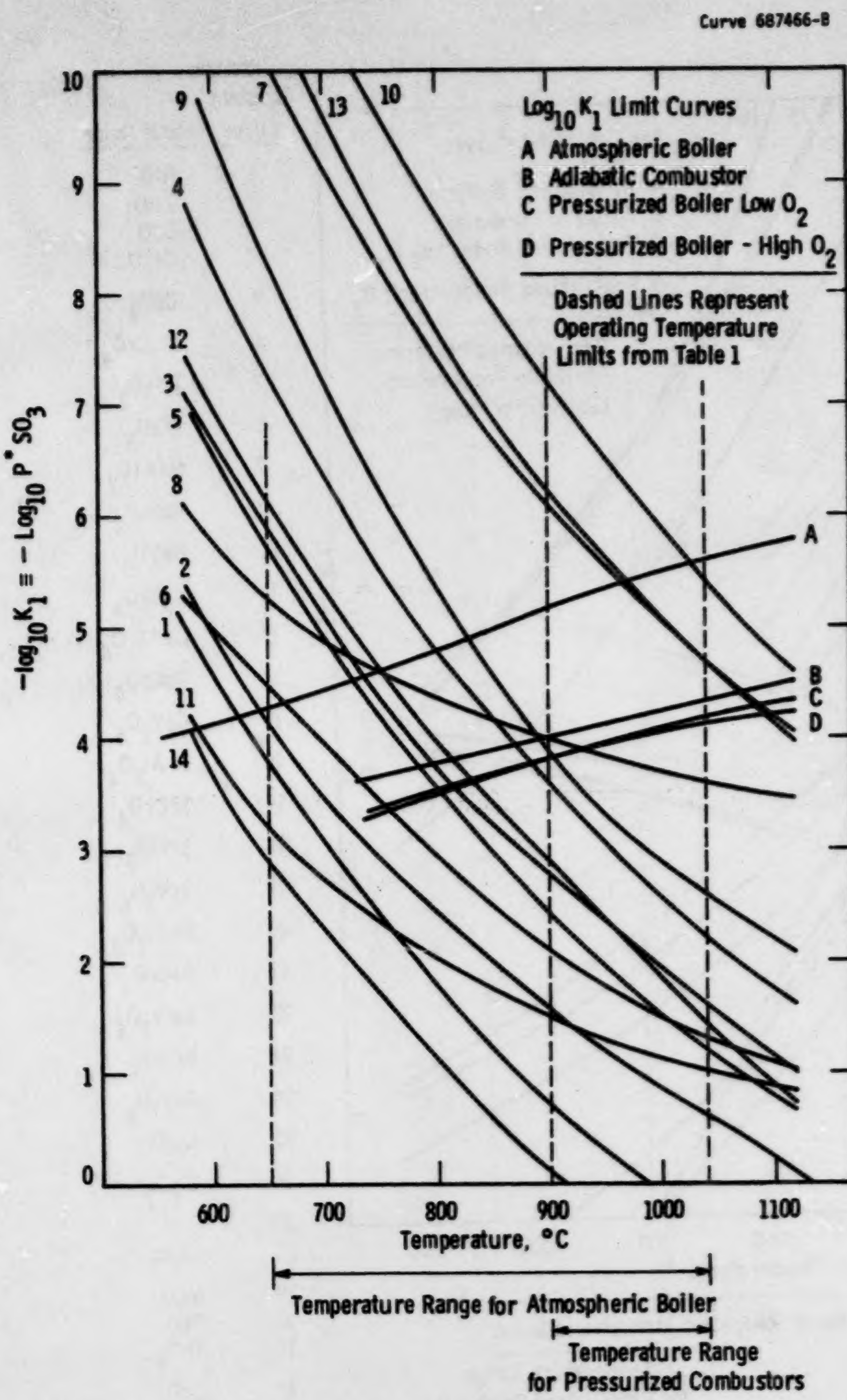
SORBENT MELTING DATA

Many sorbent physical properties are of interest (such as density, hardness, specific heat, and so forth.). Melting-point data are critical in identifying the potential operating conditions for the alternative sorbents. Melting points were collected from standard references and are listed in Table 7 for the oxide, carbonate, sulfate, and sulfide forms.[8,9]

On the basis of these data, the following metal oxides should be eliminated from further consideration since the melting point of the oxide or the sulfate is exceeded in the required temperature range identified in Table 6: K_2O, Ag_2O, Bi_2O_3, and ZrO_2. Low melting points for the components Na_2CO_3, $LiCO_3$, Na_2SO_4, PbO, CrO_3 and V_2O_5 also limit the applicability of some sorbents.

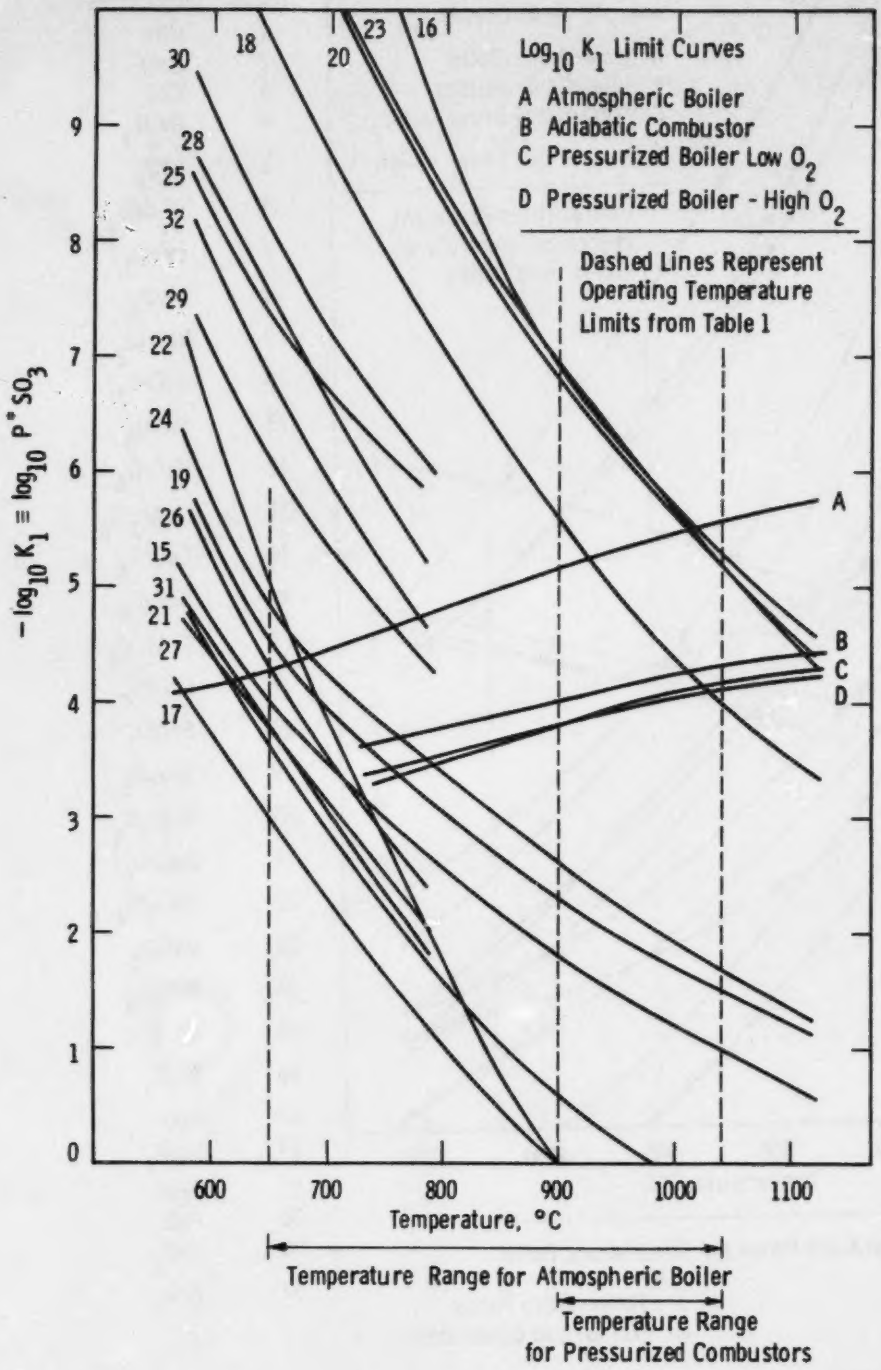
TABLE 5. LIMITING VALUES FOR THE METAL SULFATE DECOMPOSITION FOR SORBENT ACCEPTANCE

	Temp., °C	$-\log_{10} K_1 <$
Atmospheric Pressure Boiler - 4 v/o O_2	600	4.159
	650	4.291
	760	4.678
	900	5.186
	1040	5.584
Pressurized Boiler 2 v/o O_2 (low excess air)	760	3.370
	900	3.814
	1040	4.194
Pressurized Boiler 10 v/o O_2(high excess air)	760	3.438
	900	3.814
	1040	4.132
Adiabatic Combustor 16 v/o O_2	760	3.697
	900	4.015
	1040	4.343



Equilibrium Constant Curve	Metal Oxide
1	NiO
2	ZnO
3	CdO
4	Ce_2O_3
5	CeO_2
6	Li_2CrO_4
7	$LiFeO_2$
8	$LiVO_3$
9	$NaAlO_2$
10	$NaFeO_2$
11	$NaVO_3$
12	K_2CrO_4
13	$CaAl_2O_4$
14	$CaCrO_4$
15	CaV_2O_6
16	$SrAl_2O_4$
17	$SrCrO_4$
18	$SrTiO_3$
19	SrV_2O_6
20	$BaAl_2O_4$
21	$BaCrO_4$
22	$BaFe_2O_4$
23	$BaTiO_3$
24	BaV_2O_6
25	Ag_2O
26	Bi_2O_3
27	CoO
28	La_2O_3
29	MgO
30	PbO
31	ThO_2
32	ZrO_2

Figure 1 – Equilibrium constant for $MeSO_4 \rightleftarrows MeO + SO_3$



Equilibrium Constant Curve	Metal Oxide
1	NiO
2	ZnO
3	CdO
4	Ce_2O_3
5	CeO_2
6	Li_2CrO_4
7	$LiFeO_2$
8	$LiVO_3$
9	$NaAlO_2$
10	$NaFeO_2$
11	$NaVO_3$
12	K_2CrO_4
13	$CaAl_2O_4$
14	$CaCrO_4$
15	CaV_2O_6
16	$SrAl_2O_4$
17	$SrCrO_4$
18	$SrTiO_3$
19	SrV_2O_6
20	$BaAl_2O_4$
21	$BaCrO_4$
22	$BaFe_2O_4$
23	$BaTiO_3$
24	BaV_2O_6
25	Ag_2O
26	Bi_2O_3
27	CoO
28	La_2O_3
29	MgO
30	PbO
31	ThO_2
32	ZrO_2

Figure 2 — Equilibrium constant for $MeSO_4 \rightleftarrows MeO + SO_3$

TABLE 6. METAL OXIDES ACCEPTABLE BASED ON THERMODYNAMICALLY PREDICTED DESULFURIZER SO_x CONCENTRATION

Maximum temperature (°C) at which the alternative sorbent will meet the equilibrium criteria SO_x concentration (Table 1)

Metal Oxide	Atm-Pressure Boiler[a]	Pressurized Boiler[b] (high and low excess air)	Adiabatic Combustor[b]
Li_2O	1040	1040	1040
Na_2O	1040	1040	1040
K_2O	1040	1040	1040
CaO	1040	1040	1040
SrO	1040	1040	1040
BaO	1040	1040	1040
$LiAlO_2$	1040	1040	1040
Li_2TiO_3	1040	1040	1040
CdO	735	NA[c]	NA
Ce_2O_3	800	NA	NA
CeO_2	725	NA	NA
Li_2CrO_4	665	NA	NA
$LiFeO_2$	965	1040	1040
$LiVO_3$	750	930	900
$NaAlO_2$	830	905	NA
$NaFeO_2$	1030	1040	1040
K_2CrO_4	750	NA	NA
$CaAl_2O_4$	970	1040	1040
$SrAl_2O_4$	1010	1040	1040
$SrTiO_3$	925	1025	1010
SrV_2O_6	665	NA	NA
$BaAl_2O_4$	1010	1040	1040
$BaFe_2O_4$	675	NA	NA
$BaTiO_3$	1020	1040	1040
BaV_2O_6	685	NA	NA
Ag_2O[d]	870	990	970
Bi_2O_3	650	NA	NA
La_2O_3[d]	810	NA	NA
MgO	760	NA	NA
PbO[d]	870	970	960
ZrO_2	780	NA	NA

[a] Minimum operating temperature of 650°C.

[b] Minimum operating temperature of 900°C.

[c] NA = Not acceptable because maximum temperature limit is less than minimum operating temperature for the fluidized-bed combustion variation (Table 1, Column 2).

[d] Data available to 800°C extrapolated to higher temperatures.

TABLE 7. MELTING-POINT DATA

Sorbent	Melting Point (°C)			
	Oxide Form	Carbonate Form	Sulfate Form	Sulfide Form
Li_2O	1727	727	--	--
Na_2O	920	856	884	950
K_2O	$\sim$700	--	1069	--
CaO	2587	1339	1450	Decomposes
SrO	2430	1500	1605	$<$2000
BaO	1923	1740	1347	1200
CdO	Decomposes	Decomposes	1000	1750
Ce_2O_3	1687	--	Decomposes	$<$2100
CeO_2	2727	--	--	--
Ag_2O	Decomposes 187	--	--	--
Bi_2O_3	817	Decomposes	Decomposes 405	--
La_2O_3	2317	Decomposes	Decomposes 1150	2100-2150
MgO	2802	Decomposes	Decomposes	--
PbO	886	Decomposes	1170	1112
ZrO_2	2677	--	Decomposes 410	--
$LiAlO_2$	1900-2000	727	860	900-975
Li_2TiO_3	1550	727	860	900-975
Li_2CrO_4	--	727	860	900-975
$LiFeO_2$	--	727	860	900-975
$LiVO_3$	--	690	690	690
$NaAlO_2$	1800	856	884	950
$NaFeO_2$	--	856	884	950
K_2CrO_4	968	--	1069	--
$CaAl_2O_4$	1600	1339	1450	Decomposes
$SrAl_2O_4$	--	1500	1605	2045
$SrTiO_3$	--	1500	1605	1825
SrV_2O_6	--	690	690	690
$BaAl_2O_4$	--	1740	1347	1200
$BaFe_2O_4$	--	1565	1347	1200
$BaTiO_3$	--	1740	1347	1200
BaV_2O_6	--	690	690	690
Al_2O_3	2045			
TiO_2	1825			
Cr_2O_3	2435			
Fe_2O_3	1565			
V_2O_5	690			

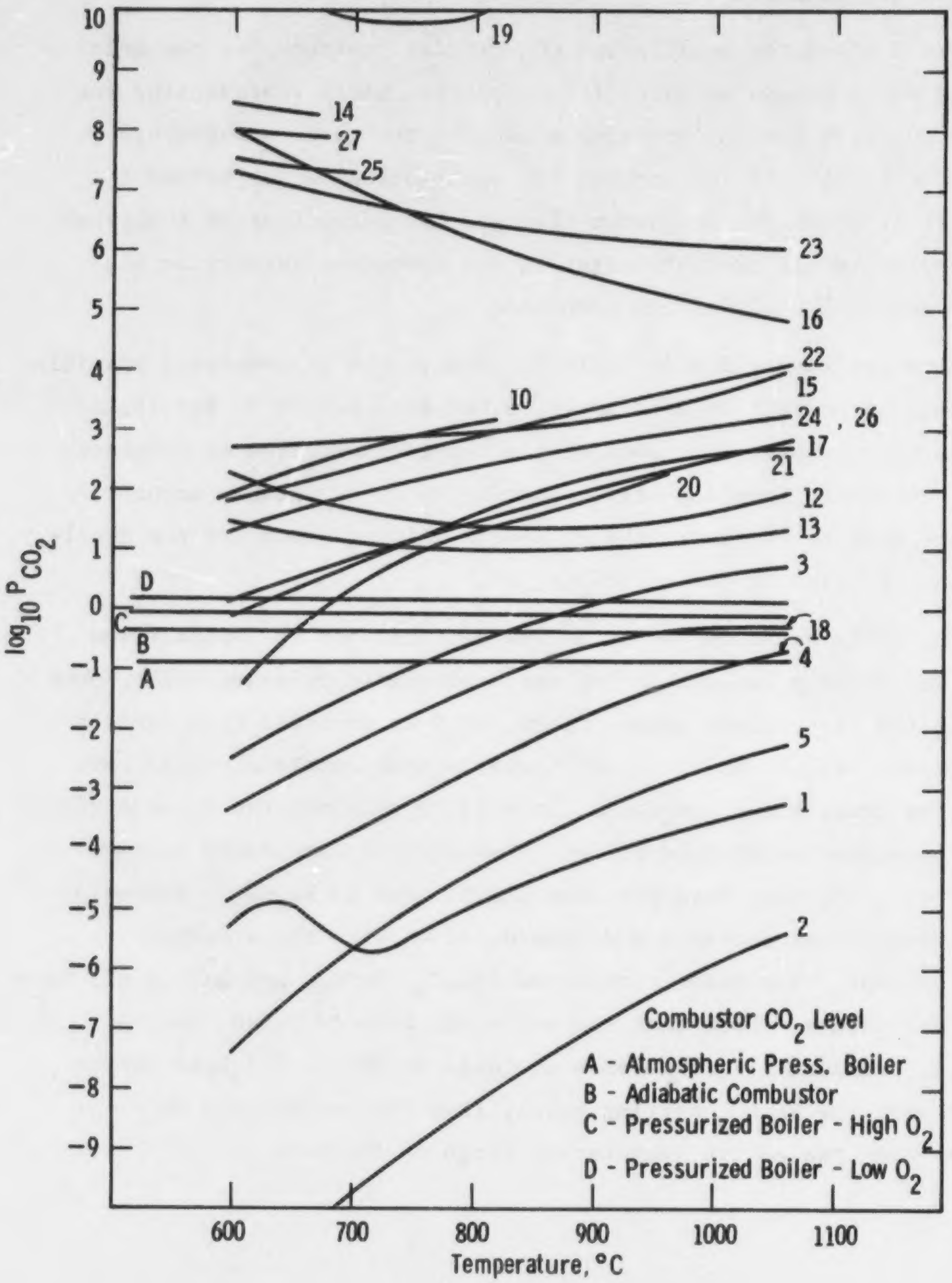
METAL CARBONATE STABILITY

Figure 3 shows the equilibrium CO_2 partial pressure for the metal carbonates which remain as potential sorbents. Lines representing the combustor CO_2 exit content are also shown for the three power cycle concepts (Table 1). If the sorbent CO_2 equilibrium curve (curves 1 through 27) is above the combustor flue gas CO_2 curve (curves A through D), the sorbent would probably exist in the combustor largely as the oxide; if below, largely as the carbonate.

Results are summarized in Table 8. Six of the 27 remaining possible sorbents may be present as carbonates rather than oxides in the fluid-bed combustor, at least over some of the temperature range of interest. While the carbonate form may still function as an acceptable sorbent, two factors must be checked: the carbonate melting point and the desulfurization potential of the carbonate.

Li_2CO_3 melts at 727°C, so it is unacceptable for the pressurized concepts and is only acceptable for the atmospheric-pressure boiler over a very limited temperature range. Thus, Li_2O is excluded from further consideration. Na_2CO_3 melts at 856°C and is then completely unacceptable for the pressurized concepts. It will be retained for consideration with the atmospheric-pressure boiler. $NaFeO_2$ when carbonated becomes $Na_2CO_3 \cdot Fe_2O_3$ and must face the same limitations as Na_2CO_3 - exclusion from the pressurized concepts and consideration with the atmospheric-pressure concept. The other carbonates ($CaCO_3$, $SrCO_3$, and $BaCO_3$) all have high melting points. Note that the carbonate form of $NaFeO_2$ in the atmospheric-pressure boiler becomes unstable at 860°C, which is almost identical with the Na_2CO_3 melting point; thus the sorbent may be acceptable over the entire temperature range of interest.

Curve 687469-B



Curve	Sorbent
1	Li_2O
2	Na_2O
3	CaO
4	SrO
5	BaO
6	CdO
7	Ce_2O_3
8	CeO_2
9	La_2O_3
10	MgO
11	PbO
12	$LiAlO_2$
13	Li_2TiO_3
14	Li_2CrO_4
15	$LiFeO_2$
16	$LiVO_3$
17	$NaAlO_2$
18	$NaFeO_2$
19	K_2CrO_4
20	$CaAl_2O_4$
21	$SrAl_2O_4$
22	$SrTiO_3$
23	SrV_2O_6
24	$BaAl_2O_4$
25	$BaFe_2O_4$
26	$BaTiO_3$
27	BaV_2O_6

Figure 3 — Metal carbonate stability

TABLE 8. METAL CARBONATE STABILITY

Sorbent (Curve in Fig. 3)		Atm-Pressure Boiler	Pressurized Boiler	Adiabatic Combustor
1	Li_2O	C[a]	C	C
2	Na_2O	C	C	C
3	CaO	760°C[b]	875°C, 910°C (Low O_2)	860°C
4	SrO	C	C	C
5	BaO	C	C	C
6	CdO	Unknown	NA[c]	NA
7	Ce_2O_3	Unknown	NA	NA
8	CeO_2	Unknown	NA	NA
9	La_2O_3	Unknown	NA	NA
10	MgO	0[d]	NA	NA
11	PbO	0	0	0
12	$LiAlO_2$	0	0	0
13	Li_2TiO_3	0	0	0
14	Li_2CrO_4	0	NA	NA
15	$LiFeO_2$	0	0	0
16	$LiVO_3$	0	0	0
17	$NaAlO_2$	0	0	NA
18	$NaFeO_2$	860°C	C	C
19	K_2CrO_4	0	NA	NA
20	$CaAl_2O_4$	0	0	0
21	$SrAl_2O_4$	0	0	0
22	$SrTiO_3$	0	0	0
23	SrV_2O_6	0	NA	NA
24	$BaAl_2O_4$	0	0	0
25	$BaFe_2O_4$	0	NA	NA
26	$BaTiO_3$	0	0	0
27	BaV_2O_6	0	NA	NA

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[a] C - Carbonate form stable.

[b] Temperature indicates carbonate decomposition point.

[c] NA - not applicable (from Table 6).

[d] O - Oxide form stable.

The equilibrium desulfurization potential of the metal carbonates will be somewhat reduced compared to the metal oxide form. For the simple oxides:

$$MeSO_4 + CO_2 \overset{K}{\rightleftharpoons} MeCO_3 + SO_3,\ K = P_{SO_3}/P_{CO_2}$$

$$MeSO_4 \overset{K_1}{\rightleftharpoons} MeO + SO_3,\ K_1 = P^*_{SO_3}$$

$$MeO + CO_2 \overset{K_2}{\rightleftharpoons} MeCO_3,\ K_2 = 1/P_{CO_2}$$

Thus, $K = K_1K_2$ and $P_{SO_3} = K_1K_2\ P^*_{CO_2}$

or

$$P_{SO_3}/P^*_{SO_3} = P^*_{CO_2}/P_{CO_2}$$

where $P^*_{SO_3}$ is the equilibrium SO_3 for the metal oxide and $P^*_{CO_2}$ is the actual partial pressure of CO_2 in the combustor (Table 1). K_1 is the metal oxide equilibrium constant in Figures 1 and 2, P_{SO_3} is the equilibrium SO_3 partial pressure for the carbonated sorbent, and P_{CO_2} is the equilibrium CO_2 partial pressure for the sorbent in Figure 3. Then,

$$\log_{10} P_{SO_3} - \log_{10} P^*_{SO_3} = \log_{10} K - \log_{10} K_1 = \log_{10}\left(\frac{P^*_{CO_2}}{P_{CO_2}}\right).$$

The effect of carbonate stability on the desulfurization potential may be predicted from the curves in Figures 1 and 2 (giving $\log_{10} P^*_{SO_3}$) and the ratio $P^*_{CO_2}/P_{CO_2}$ from Figure 3 (giving $\log_{10} P_{CO_2}$) and Table 1 (giving $P^*_{CO_2}$).

For the complex oxide forms only $NaFeO_2$ is of interest. For $NaFeO_2$:

$$2\ NaFeO_2 + SO_3 \underset{}{\overset{K_1}{\rightleftharpoons}} Na_2SO_4 + Fe_2O_3$$

$$2\ NaFeO_2 \overset{K_2}{\rightleftharpoons} Na_2O + Fe_2O_3$$

$$Na_2O + CO_2 \overset{K_3}{\rightleftharpoons} Na_2CO_3$$

$$Na_2O + SO_3 \overset{K_4}{\rightleftharpoons} Na_2SO_4$$

and

$$2\ NaFeO_2 + CO_2 \overset{K_2K_3}{\rightleftharpoons} Na_2CO_3 + Fe_2O_3$$

$$Na_2CO_3 + Fe_2O_3 + SO_3 \overset{K_1/K_2K_3}{\rightleftharpoons} Na_2SO_4 + Fe_2O_3 + CO_2 \ .$$

Thus,

$$P_{SO_3} = \frac{K_2K_3}{K_1}\ P^*_{CO_2} = \frac{K_3}{K_4}\ P^*_{CO_2}$$

and

$$P_{SO_3}/P^*_{SO_3} = P^*_{CO_2}/P_{CO_2} \ ,$$

which is the same form as for the simple metal oxides.

Table 9 gives the quantity $\log_{10}K - \log_{10}K_1$ for the five sorbents of interest. Comparison with Figure 1 shows that the desulfurization potential of these metal carbonates is acceptable. $\text{Log}_{10}K$ for $NaFeO_2$ does not drop below the limit curves in Figure 1. Since $-\log_{10}K_1 >> 10$ for CaO, Na_2O, SrO and BaO (not shown in Figures 1 and 2), they are not greatly effected by carbonation.

TABLE 9. METAL CARBONATE DESULFURIZATION POTENTIAL

	$\log_{10} K - \log_{10} K_1 = \log_{10} P_{SO_3} - \log_{10} P^*_{SO_3}$				
	Temperature (°C)				
	627	727	827	927	1027
Na_2CO_3					
Atm-Pressure Boiler	10.2	8.4	7.0	5.8	4.7
$CaCO_3$					
Atm-Pressure Boiler	1.3	0.3	--	--	--
Pressurized Boiler	2.4	1.4	0.6	--	--
Adiabatic Combustor	1.8	0.8	0.0	--	--
$SrCO_3$					
Atm-Pressure Boiler	3.6	2.6	1.5	0.6	0
Pressurized Boiler	4.7	3.7	2.6	1.7	1.0
Adiabatic Combustor	4.1	3.1	2.0	1.1	0.5
$BaCO_3$					
Atm-Pressure Boiler	6.0	4.4	3.2	2.2	1.5
Pressurized Boiler	7.1	5.5	4.3	3.3	2.6
Adiabatic Combustor	6.5	4.9	3.7	2.7	2.0
$NaFeO_2$					
Atm-Pressure Boiler	2.1	1.1	0.2	--	--

SULFITE STABILITY

Sulfite stability consideration does not affect the acceptability of the sorbents. On the basis of existing data, all of the sulfites appear unstable at the conditions of interest.[5]

SUMMARY OF DESULFURIZATION POTENTIAL

Table 10 summarizes the screening results for alternative sorbent desulfurization potential. The maximum operable desulfurizer temperature is listed for the atmospheric boiler, the pressurized boiler, and the adiabatic combustor. The sorbent form listed in Table 10, oxide or carbonate, is the form projected to be stable in the combustor at the temperature maximum tabulated.

Many of the alternative sorbents in Table 10 are of limited interest because they have a limited operable temperature, may be very limited in supply,or are toxic. These sorbents are summarized in Table 11 and are excluded from further evaluation. They are reserved for further assessment if new information becomes available which indicates merit for any of them. The remaining 14 potential sorbents listed in Table 11 are the subject of the evaluation to follow. They are listed as the form stable in the combustor.

TABLE 10. SUMMARY OF ACCEPTABLE SORBENTS BASED ON DESULFURIZATION PERFORMANCE

Sorbent	Maximum Combustor Operating Temperature, °C		
	Atm-Pressure Boiler	Pressurized Boiler	Adiabatic Combustor
Na_2CO_3	856[a]	NA[a]	NA[a]
CaO	1040	1040	1040
$CaCO_3$	760[b]	910[b] (low O_2)	NA[b]
$SrCO_3$	1040	1040	1040
$BaCO_3$	1040	1040	1040
CdO[d]	735[c]	NA[c]	NA[c]
Ce_2O_3[d]	800[c]	NA[c]	NA[c]
CeO_2[d]	725[c]	NA[c]	NA[c]
La_2O_3[d]	810[c]	NA[c]	NA[c]
MgO	760[c]	NA[c]	NA[c]
PbO	870[c]	NA[a]	NA[a]
$LiAlO_2$	1040	1040	1040
Li_2TiO_3	1040	1040	1040
Li_2CrO_4	665[c]	NA[c]	NA[c]
$LiFeO_2$	965[c]	1040[c]	1040[c]
$LiVO_3$	690[a]	NA[a]	NA[a]
$NaAlO_2$	830[c]	NA[a]	NA[a,c]
$NaCO_3 \cdot Fe_2O_3$	860[c]	NA[a]	NA[a]
$CaAl_2O_4$	970[c]	1040	1040
$SrAl_2O_4$	1010[c]	1040	1040
$SrTiO_3$	925[c]	1025[c]	1010[c]
$SrV2_2O_6$	665[c]	NA[c]	NA[c]
$BaAl_2O_4$	1010[c]	1040	1040
$BaFe_2O_4$	675[c]	NA[c]	NA[c]
$BaTiO_3$	1020[c]	1040	1040
BaV_2O_6	685[c]	NA[c]	NA[c]

NA - Not acceptable.

[a] Based on melting point.

[b] Based on carbonate stability.

[c] Based on desulfurization potential (see Table 6).

[d] Insufficient information on carbonate stability.

TABLE 11. ASSESSMENT OF ACCEPTABLE SORBENTS BASED ON DESULFURIZATION PERFORMANCE

Sorbents that Merit Further Consideration:

Na_2CO_3

$CaO/CaCO_3$

$SrCO_3$

$BaCO_3$

$LiAlO_2$

$LiFeO_2$

$NaAlO_2$

$NaCO_3 \cdot Fe_2O_3$

$CaAl_2O_4$

$SrAl_2O_4$

$SrTiO_3$

$BaAl_2O_4$

$BaTiO_3$

Li_2TiO_3

Sorbents That Are Reserved for Further Consideration:

CdO	a
Ce_2O_3	b
CeO_2	a
La_2O_3	b
MgO	a
PbO	c
Li_2CrO_4	a
$LiVO_3$	a
SrV_2O_6	a
$BaFe_2O_4$	a
BaV_2O_6	a

a - Limited temperature range; could not reach advanced steam conditions; may be given further consideration at future time.

b - Probable high cost or low availability.

c - Toxic.

SECTION 6

PROJECTIONS OF SORBENT REGENERATION POTENTIAL

The regeneration potential of the selected sorbents listed in Table 11 has been projected. Thermal decomposition, reductive decomposition, and a pair of two-step processes are evaluated.

THERMAL DECOMPOSITION

Examination of Figures 1 and 2 indicates that none of the sorbents can utilize thermal decomposition as a means of regeneration within the permissible temperature range. Since $-\log_{10} P_{SO_3}$ is larger than 1.4 for all of the acceptable sorbents in Table 11, the SO_2 concentration would be too low (less than 4 mole %) to satisfy the regeneration criteria in Table 2.

REDUCTIVE DECOMPOSITION

The regeneration scheme,

$$MeSO_4 + \left\{\begin{matrix} H_2 \\ CO \end{matrix}\right\} \rightleftharpoons MeO + \left\{\begin{matrix} H_2O \\ CO_2 \end{matrix}\right\} + SO_2$$

will occur by using the in situ partial oxidation of coal to supply the reductants. The use of clean fuels such as natural gas and No. 2 fuel oil has been excluded. If it is assumed that the sulfidation reaction

$$MeSO_4 + 4\left\{\begin{matrix} H_2 \\ CO \end{matrix}\right\} \rightleftharpoons MeS + 4\left\{\begin{matrix} H_2O \\ CO_2 \end{matrix}\right\}$$

is also in equilibrium, the equilibrium SO_2 concentration may be projected by examining the reaction equilibrium for the overall reaction

$$3\ MeSO_4 + MeS \rightleftharpoons 4\ MeO + 4\ SO_2\ .$$

For the sorbents in which the carbonate form is stable, the corresponding reaction is

$$3\ MeSO_4 + MeS + 4\ CO_2 \rightleftharpoons 4\ MeCO_3 + 4\ SO_2 \quad .$$

Table 12 and Figures 4 and 5 summarize the equilibrium data and the minimum temperatures required to produce 4 volume percent SO_2 (the minimum acceptance criterion in Table 2) and 10 volume percent SO_2, both at 100 kPa and at 1000 kPa pressure. For the sorbents that are stable carbonates, a 15 percent CO_2 concentration has been assumed. The melting-point limit is also listed for each sorbent in Table 12. Two of the sorbents require a temperature exceeding the melting-point limit (and also exceeding the maximum allowable regenerator temperature of 1400°C) in order to achieve the minimum acceptable SO_2 concentration of 4 volume percent (Table 2). These sorbents, Na_2O and BaO, must be dropped from consideration for reductive decomposition. In addition, Li_2TiO_3 is not suitable for regeneration by reductive decomposition at 1000 kPa pressure because the required temperatures at that pressure are above the sorbent melting point. For three of the stable carbonate sorbents (based on desulfurizer conditions) - $CaCO_3$, $SrCO_3$, and $BaCO_3$ - the carbonate forms are not stable in 15 percent CO_2 at a temperature sufficiently high to achieve 4 percent SO_2 and must be dropped. The ultimate conclusion from Table 12 is that the barium-based alternative sorbent (BaO or $BaCO_3$) is not suitable for regeneration by reductive decomposition. The other sorbents in either the oxide or carbonate form are suitable for the temperature ranges listed in Table 12.

TWO-STEP REGENERATION SCHEMES

The reaction equilibrium for the first step of the two-step schemes,

$$MeSO_4 + 4\left\{\begin{matrix} H_2 \\ CO \end{matrix}\right\} \rightleftharpoons MeS + 4\left\{\begin{matrix} H_2 \\ CO \end{matrix}\right\}$$

and

$$MeSO_4 + \left\{\begin{matrix} H_2 \\ CO \end{matrix}\right\} \rightleftharpoons MeO + \left\{\begin{matrix} H_2O \\ CO_2 \end{matrix}\right\} + SO_2$$

TABLE 12. REGENERATION BY REDUCTIVE DECOMPOSITION

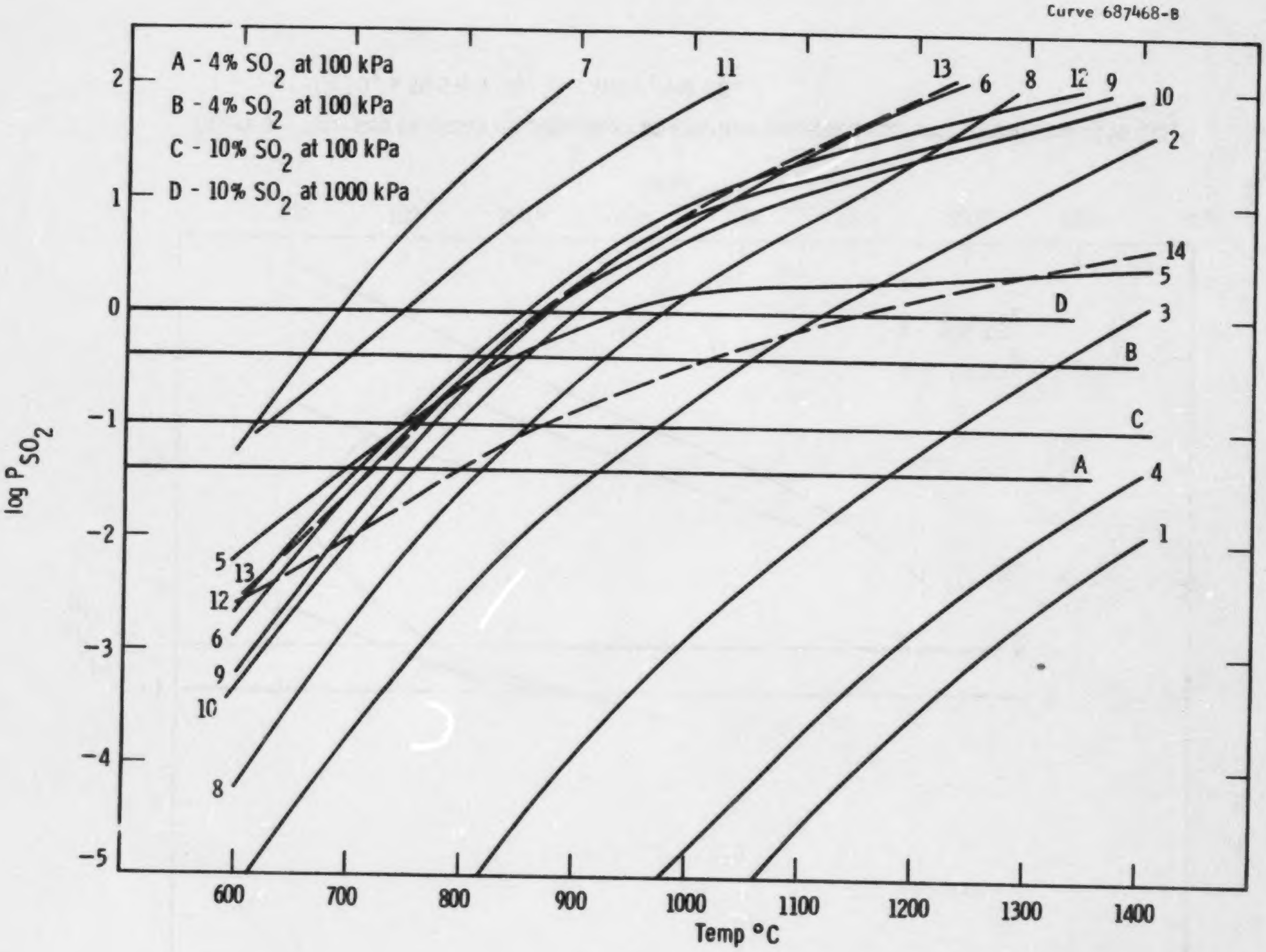
$3\ MeSO_4 + MeS \rightleftarrows 4\ MeO + 4\ SO_2$			Atmospheric Pressure Minimum Temperature for °C		Pressurized Operation Minimum Temperature for °C	
Sorbent[a]	Curve (Fig. 4)	Melting Limit, °C	4% SO_2	10% SO_2	4% SO_2	10% SO_2
Na_2O[b]	1	884	>1400	>1400	NA[c]	NA
CaO	2	1450	920	975	1060	1120
SrO	3	1605	1180	1235	1330	1390
BaO[b]	4	1347	1400	>1400	>1400	>1400
$LiAlO_2$	5	860	700	750	850	940[b]
$LiFeO_2$	6	860	720	760	820	880[b]
$NaAlO_2$	7	884	590	620	NA	NA
$NaFeO_2$	8	884	820	860	NA	NA
$CaAl_2O_4$	9	1450	740	770	830	880
$SrAl_2O_4$	10	1605	760	800	860	900
$SrTiO_3$	11	1605	580	630	700	750
$BaAl_2O_4$	12	1347	710	750	810	860
$BaTiO_3$	13	1347	720	760	820	870
Li_2TiO_3	14	860	800	870[b]	1020[b]	1150[b]
$3\ MeSO_4 + MeS + 4\ CO_2 \rightleftarrows 4\ MeCO_3 + 4\ SO_2$ (Fig. 5)						
Na_2CO_3	1	856	740	860	NA	NA
$CaCO_3$[b]	2	1339	NS[d]	NS	NS	NS
$SrCO_3$[b]	3	1500	NS	NS	NS	NS
$BaCO_3$[b]	4	1347	NS	NS	NS	NS
$Na_2CO_3 \cdot Fe_2O_3$	8	856	690	840	NA	NA

[a] Form of sorbent product from regeneration process.

[b] Dropped from consideration for reductive decomposition because minimum temperature >1400°C.

[c] NA - Not acceptable desulfurizer performance (Table 10).

[d] NS - Carbonate form not stable in 15% CO_2 to sufficiently high temperature to achieve 4% SO_2.



Curve	Sorbent
1	Na_2O
2	CaO
3	SrO
4	BaO
5	$LiAlO_2$
6	$LiFeO_2$
7	$NaAlO_2$
8	$NaFeO_2$
9	$CaAl_2O_4$
10	$SrAl_2O_4$
11	$SrTiO_3$
12	$BaAl_2O_4$
13	$BaTiO_3$
14	Li_2TiO_3

Figure 4 – One-step reductive decomposition equilibrium SO_2 projection - no sorbent carbonation $3\,MeSO_4 + MeS \rightleftarrows 4MeO + 4\,SO_2$

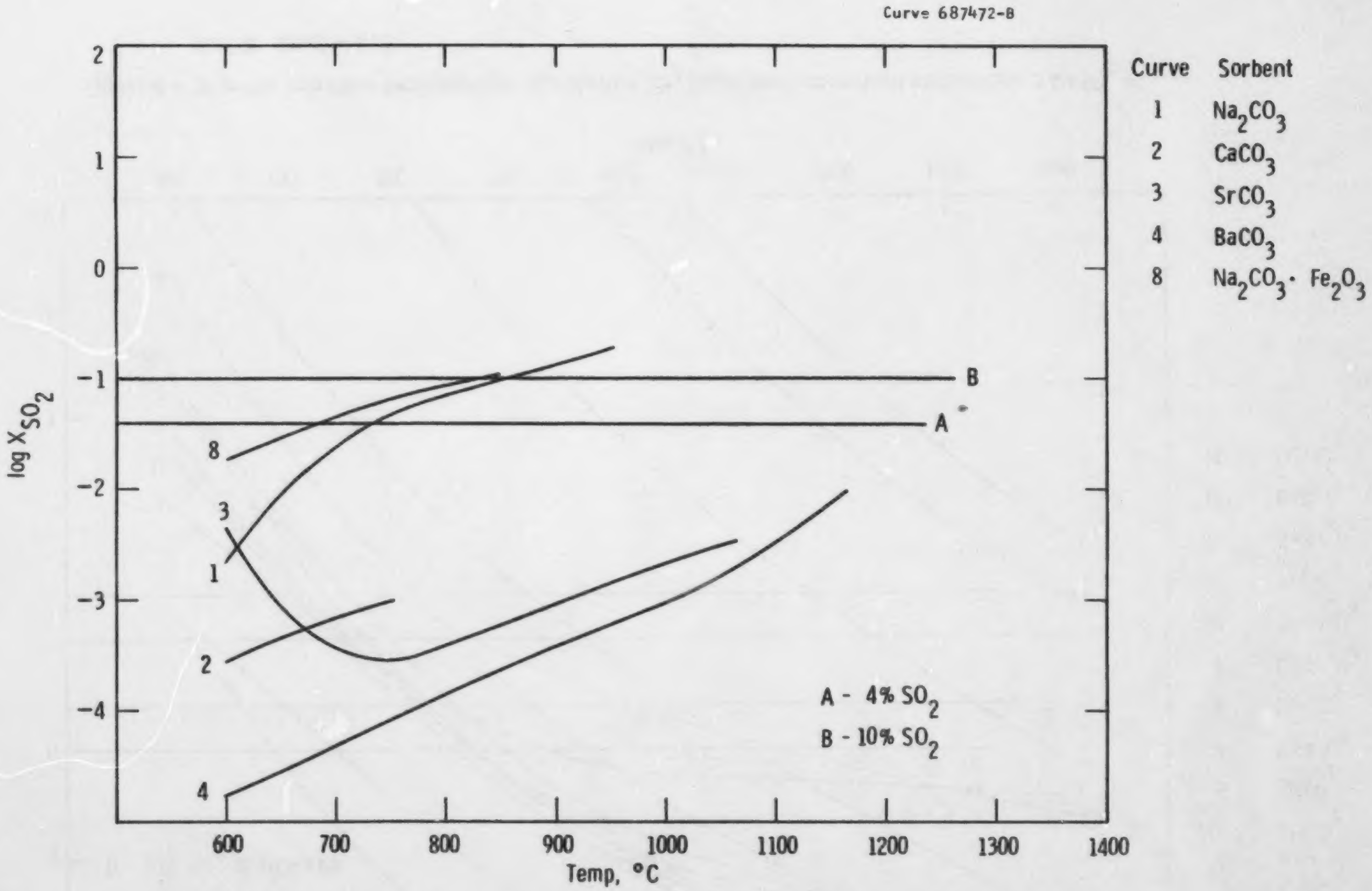


Figure 5 – One-step reductive decomposition equilibrium projection - sorbent carbonation (15% CO_2)

$$3MeSO_4 + MeS + 4\ CO_2 \rightleftarrows 4\ MeCO_3 + 4\ SO_2$$

may be evaluated by considering again the overall reaction

$$3\ MeSO_4 + MeS \rightleftharpoons 4\ MeO + 4\ SO_2\ .$$

The maximum regenerator temperature for MeS generation with a resulting low SO_2 emission ($X_{SO_2} \leq 10^{-4}$ in Table 2 is given in Table 13 and is based on the curves in Figures 3 and 4. Many of the sorbents require very low regenerator temperatures in order to satisfy this requirement (500°C). Reaction kinetics may limit the reduction step of the two-step process in some cases. None of the sorbents is eliminated on the basis of the sulfide formation step, but the kinetics of this step must be explored at these low temperatures to see if the reaction rates are acceptable.

The metal sulfide produced in the sulfate reduction step may be treated by either of two schemes:

$$MeS + H_2O \rightleftharpoons MeO + H_2S$$

or

$$MeS + H_2O + CO_2 \rightleftharpoons MeCO_3 + H_2S\ .$$

Table 14 and Figure 6 consider the first reacting scheme. Equilibrium data are shown in Figure 6. Figure 6 also indicates two curves (A and B) based on mass balances, giving the mole fraction of H_2S as a function of X_{H_2S}/X_{H_2O} for two initial mole fractions of steam of 1.0 and 0.5; the temperature required to obtain greater than 3 mole % H_2S (the minimum acceptance criterion) and 10 mole % H_2S may be obtained from the figure and is listed in Table 14 for the case where the reactant gas is 100 percent steam. The maximum possible H_2S mole fraction is also projected in the table. Because four of the sorbents require a temperature exceeding the melting-point limit and/or the maximum operable temperature of 1400°C, they are dropped from consideration for this reaction scheme.

TABLE 13. METAL SULFIDE FORMATION

$3\ MeSO_4 + MeS \rightleftarrows 4\ MeO + 4\ SO_2$

	CRITERION - $X_{SO_2} < 10^{-4}$		
Sorbent	Curve (Fig. 4)	100 kPa Pressure Maximum Temperature, °C	1000 kPa Pressure Maximum Temperature, °C
Na_2O[a]	1	1150	NA[b]
CaO	2	680	760
SrO	3	890	990
BaO[c]	4	1070	1180
$LiAlO_2$	5	<<600	<<600
$LiFeO_2$	6	520	590
$NaAlO_2$	7	<<600	NA
$NaFeO_2$	8	615	NA
$CaAl_2O_4$	9	540	615
$SrAl_2O_4$	10	550	625
$SrTiO_3$	11	<<600	<<600
$BaAl_2O_4$	12	<580	580
$BaTiO_3$	13	<550	550
Li_2TiO_3	14	<<600	$\sim$500
	(Fig. 5)		
Na_2CO_3	1	<600	NA
$CaCO_3$	2	<600	750
$SrCO_3$	3	d	910
$BaCO_3$	4	770	1000
$Na_2CO_3 \cdot Fe_2O_3$	8	<<600	NA

[a] Melting limit of 884°C.

[b] NA - Not acceptable (see Table 10).

[c] Melting limit of 1200°C.

[d] See curve in Figure 5 for exceptional behavior.

TABLE 14. H_2S GENERATION FROM METAL SULFIDE BY $MeS + H_2O \rightleftarrows MeO + H_2S$[a]

Sorbent	Curve (Fig. 6)	Temperature, °C for X_{H_2S} of		Melting Limit, °C	Maximum X_{H_2S}	Temperature, °C for Maximum H_2S
		>0.03	>0.10			
Na_2O[b]	1	>1400	>1400	920	---	---
CaO[b]	2	>1400	>1400	1450	---	---
SrO[b]	3	>1400	>1400	1605	---	---
BaO[b]	4	>1400	>1400	1200	---	---
$LiAlO_2$	5	<1300	<1300	860	>0.9	<1150
$LiFeO_2$	6	>700	>980	860	0.10	975
$NaAlO_2$	7	<1300	<1300	884	0.40	950
$NaFeO_2$	8	>800	>1160	884	0.06	950
$CaAl_2O_4$	9	>700	---	1450	0.10	950
$SrAl_2O_4$	10	<1300	<1300	1605	0.60	800
$SrTiO_3$	11	<1300	<1300	1605	>0.9	<1150
$BaAl_2O_4$	12	<1300	<1300	1200	>0.9	<950
$BaTiO_3$	13	<1300	<1300	1200	>0.9	<800
Li_2TiO_3	14	<1300	<1300	860	>0.9	<900

[a] Basis - reactant is 100% steam.

[b] Drop from consideration for regeneration by this reaction.

Curve 687471-B

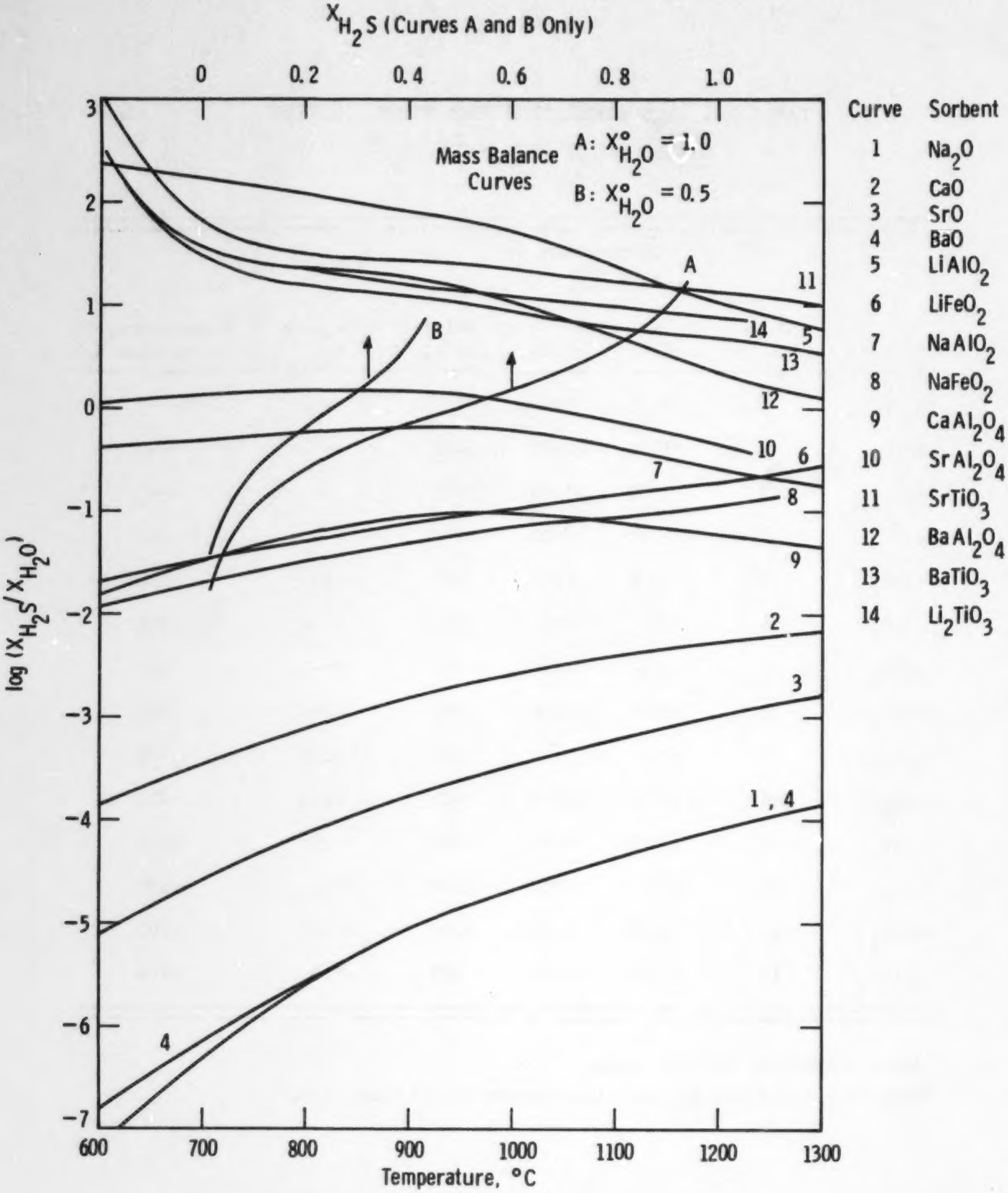


Figure 6 — $MeS + H_2O \rightleftarrows MeO + H_2S$ reaction equilibrium

For reaction with steam and CO_2, equilibrium data are shown in Figure 7 for a reaction mixture of 50 percent H_2O and 50 percent CO_2 for the eight sorbents which will form stable carbonates (see Figure 3). Curves A and B in Figure 7 show H_2S levles based upon mass balance. Table 15 projects the temperature required for 3 and 10 percent H_2S at 100 kPa and at 1000 kPa. For this reaction scheme the equilibrium H_2S increases as the temperature decreases, so there is no apparent maximum H_2S limit. Kinetic limitations will control in the actual case. None of the possible sorbents being considered is excluded for this reaction scheme.

SUMMARY OF REGENERATION POTENTIAL

Tables 13 and 17 summarize the equilibrium projections for desulfurization and regeneration. Table 16 considers the atmospheric-pressure system and Table 17 considers the pressurized system. For those sorbents that may be stable carbonates under some operating conditions, the behavior of both the oxide and carbonate forms are indicated in the summary tables in order to permit identification of transition points from oxide to carbonate forms.

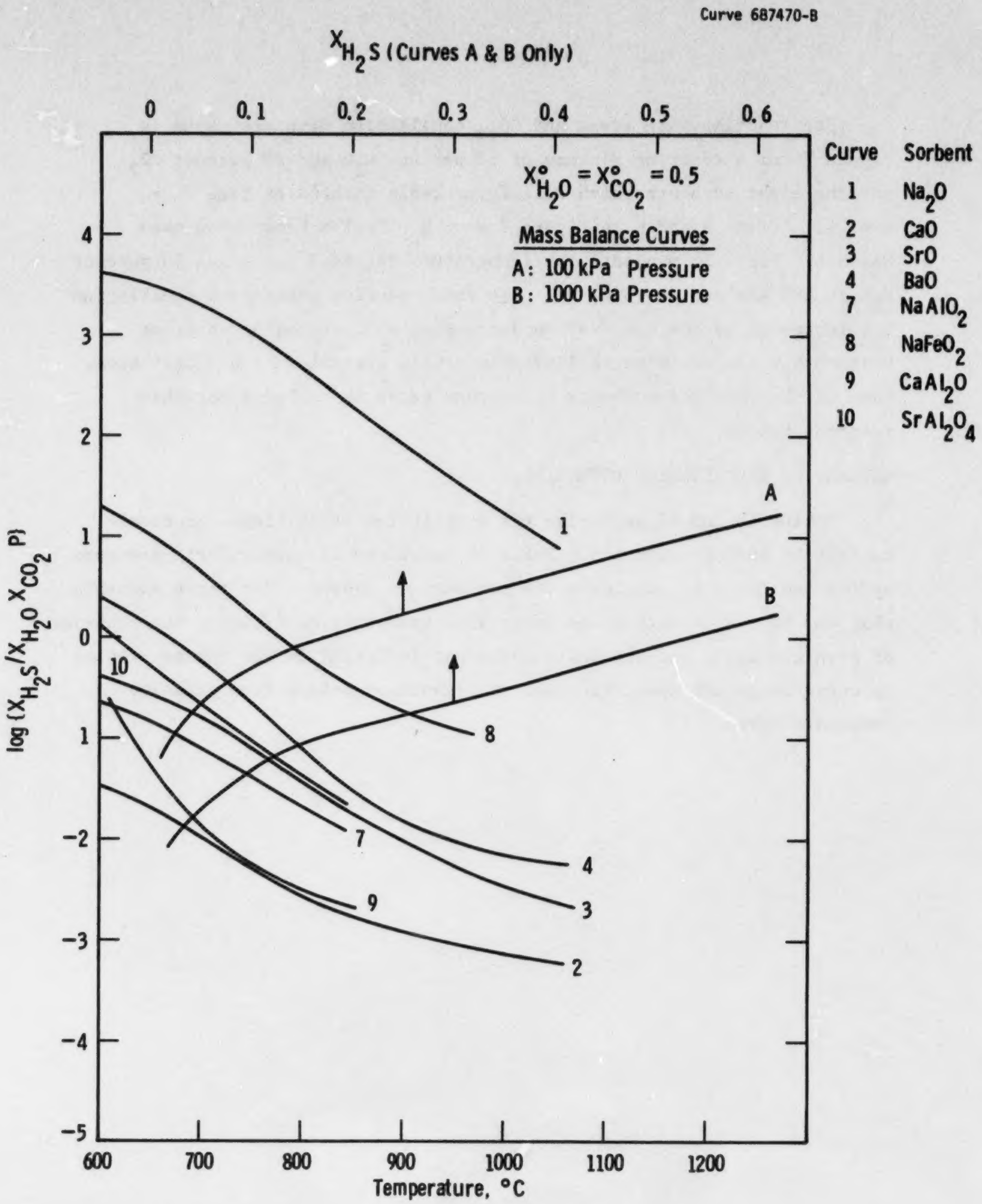


Figure 7 — $MeS + H_2O + CO_2 \rightleftarrows MeCO_3 + H_2S$ reaction equilibrium

TABLE 15. H_2S GENERATION FROM METAL SULFIDE[a] BY $MeS + H_2O + CO_2 \rightleftharpoons Me\ CO_3 + H_2S$[b]

Sorbent	Curve (Fig. 7)	100 kPa Pressure Temperature, °C, for X_{H_2S} of		1000 kPa Pressure Temperature, °C, for X_{H_2S} of		Melting Limit, °C
		>0.03	>0.10	>0.03	>0.10	
Na_2O	1	<1300	<1200	<1300	<1300	856
CaO	2	<500	<<500	<690	<600	1339
SrO	3	<720	<600	<880	<780	1500
BaO	4	<780	<710	<920	<820	1200
$NaAlO_2$	7	<670	<500	<840	<740	856
$NaFeO_2$	8	<950	<820	<1300	<1200	856
$CaAl_2O_4$	9	<630	<600	<700	<650	1339
$SrAl_2O_4$	10	<730	<650	<850	<790	1500

[a] No limit on the maximum X_{H_2S} for this reaction.

[b] Basis - reactance is 50% H_2O and 50% CO_2.

TABLE 16. THERMODYNAMIC SCREENING OF AFBC SORBENTS

Atmospheric-Pressure Sorbent[a]	Maximum Desulfurizer Temperature, °C[b]	One-Step Regeneration Reductive Decomposition Minimum Temperature		Two-Step Regeneration				
				1st-Step Maximum Temperature, °C	2nd-Step with Steam		2nd-Step with Steam & CO_2 Temperature (°C) for	
		4% SO_2	10% SO_2		Temperature H_2S > 3%	Maximum H_2S,%	H_2S > 3%	H_2S > 10%
Na_2O	NS[c]	NA[d]	NA	NS	NA	NA	NS	NS
Na_2CO_3	856	740	NA	665	NS	NS	<856	<856
CaO	1040	920	975	760	NA	NA	NS	NS
$CaCO_3$	760	NS	NS	750	NS	NS	<500	<<500
SrO	NS	1180	1235	NS	NA	NA	NS	NS
$SrCO_3$	1040	NS	NS	910	NS	NS	<720	<600
BaO	NS	NA	NA	NS	NA	NA	NS	NS
$BaCO_3$	1040	NS	NS	1000	NS	NS	<780	<710
$LiAlO_2$	1040	700	750	500	<1300	>90	CNS[e]	CNS
$LiFeO_2$	965	720	760	590	>700	10	CNS	CNS
Li_2TiO_3	1040	800	NA	500	<1300	>90	CNS	CNS
$NaAlO_2$	830	590	620	500	<1300	40	NS	NS
$Na_2CO_3 \cdot Al_2O_3$	NS	NS	NS	NS	NS	NS	<670	<500
$NaFeO_2$	NS	820	860	685	>800	6	NS	NS
$Na_2CO_3 \cdot Fe_2O_3$	860	690	840	<500	NS	NS	<856	<856
$CaAl_2O_4$	970	740	770	615	>700	10	NS	NS
$CaCO_3 \cdot Al_2O_3$	NS	NS	NS	NS	NS	NS	<630	<600
$SrAl_2O_4$	1010	760	800	625	<1300	60	NS	NS
$SrCO_3 \cdot Al_2O_4$	NS	NS	NS	NS	NS	NS	<730	<650
$SrTiO_3$	925	580	630	<500	<1300	>90	CNS	CNS
$BaAl_2O_4$	1010	710	750	580	<1300	>90	CNS	CNS
$BaTiO_3$	1020	720	760	550	<1300	>90	CNS	CNS

[a] Represents sorbent forms at each step of the regenerative cycle.

[b] Minimum temperature of 650°C in the desulfurizer, maximum 1040°C.

[c] NS - Sorbent in column 1 not stable form.

[d] NA - Not acceptable.

[e] CNS - Carbonate form of sorbent in column 1 not stable.

TABLE 17. THERMODYNAMIC SCREENING OF PFBC SORBENTS

Pressurized Sorbent[a]	Maximum Desulfurizer Temperature, °C[b]	One-Step Regeneration Reductive Decomposition Minimum Temperature		Two-Step Regeneration				
				1st-Step Maximum Temperature, °C	2nd-Step with Steam		2nd-Step with Steam & CO2 Temperature (°C) for	
		4% SO_2	10% SO_2		Temperature H_2S > 3%	Maximum H_2S (%)	H_2S > 3%	H_2S > 10%
CaO	1040	1060	1120	NS[c]	NA[d]	NA	NS	NS
$CaCO_3$	910[e]/NA[f]	NS	NS	750	NS	NS	<690	<600
SrO	NS	1330	1390	1100	NA	NA	NS	NS
$SrCO_3$	1040	NS	NS	910	NS	NS	<880	<780
BaO	NS	NA	NA	1200	NA	NA	NS	NS
$BaCO_3$	1040	NS	NS	1170	NS	NS	<920	<820
$LiAlO_2$	1040	850	NA	620	<1300	>90	CNS[g]	CNS
$LiFeO_2$	1040	820	NA	670	>700	10	CNS	CNS
Li_2TiO_3	1040	NA	NA	700	<1300	>90	CNS	CNS
$CaAl_2O_4$	1040	830	880	690	>700	10	NS	NS
$CCO_3 \cdot Al_2O_3$	NS	NS	NS	NS	NS	NS	<700	<650
$SrAl_2O_4$	1040	860	900	710	<1300	60	NS	NS
$SrCO_3 \cdot Al_2O_3$	NS	NS	NS	NS	NS	NS	<850	<790
$SrTiO_3$	1025[e]/1010[f]	700	750	500	<1300	>90	CNS	CNS
$BaAl_2O_4$	1040	810	860	650	<1300	>90	CNS	CNS
$BaTiO_3$	1040	820	870	660	<1300	>90	CNS	CNS

[a] Represents sorbent forms at each step of the regenerative cycle.

[b] Minimum temperature of 900°C in the desulfurizer, maximum 1040°C.

[c] NS - Sorbent in column 1 not stable form.

[d] NA - Not acceptable.

[e] Pressurized boiler only.

[f] Adiabatic combustor only.

[g] CNS - Carbonate form of Sorbent in column 1 not stable.

SECTION 7

MATERIAL AND ENERGY BALANCE LIMITATIONS

Generalized material and energy balance relationships were developed for the regeneration schemes to identify any sorbents that might be limited in performance because of material and energy balance constraints. Such constraints may arise in practice when the method of supplying the energy needs of the reaction scheme (e.g., in situ combustion of coal, preheat of reactant streams) or controlling the reactor temperature simultaneously dilutes the reactor product to a low level of SO_2 or H_2S.

There are a large number of variables and parameters that affect the material and energy balances: the sorbent properties and heats of reaction, the reaction temperature, the extent of reaction, the extent of competing reactions, the mass ratio of support material to sorbent material in the sorbent structure, the sorbent circulation rate, reactant streams preheat temperature, and so on. After the effects of these variables and parameters were examined in detail by computer analysis for some of the sorbents,it was found that the regenerator performance could range from unacceptable to acceptable for a large number of combinations of these variables. A set of operating conditions and assumed operating parameters and performance variables exist for each of the sorbents that could lead to optimum regenerator performance (e.g., maximum SO_2 or H_2S concentration), but a set also exists that could lead to unacceptable regenerator performance. Material and energy balances could be used to identify these sets of operating conditions and performance variables; but due to the large number of parameters involved,this is more logically conducted in parallel with an experimental program that measures critical performance factors. The general material and energy balances, in the absence of data, will not lead to the elimination of any of the alternative sorbents from consideration.

In terms of projecting the potential of the alternative sorbents, material balances around the regenerator have been used to project the maximum possible performance levels. Energy balances have been excluded from general consideration in keeping with the previous remarks.

REDUCTIVE DECOMPOSITION

For the reductive decomposition regeneration scheme the number of moles of carbon consumed in the regenerator per mole of SO_2 produced is given by

$$\frac{N_C}{N_{SO_2}} = \frac{1/2\ (1 + 4(N_{MeS}/N_{SO_2})/(1 + 1/4\ \alpha))}{1 - \xi} ,$$

assuming that all of the coal fed to the regenerator is completely consumed and complete combustion or reaction of the generated CO and H_2 occurs. N_{MeS}/N_{SO_2} is the number of moles of metal sulfide produced per mole of SO_2 generated in the regenerator by the competing reaction, α is the molal ratio of carbon to hydrogen in the coal, and ξ is the fraction of stoichiometric air/fuel ratio used in the regenerator for partial coal combustion. Assuming that $N_{MeS}/N_{SO_2} = 0$, $\alpha = 1.1$, and that the minimum value of ξ that can be used (due to tar formation and carbon losses) is 0.5 (50 percent of the stoichiometric air/fuel ratio), then the minimum value for N_C/N_{SO_2} is 0.81. For comparison, the moles of carbon consumed in the fluid-bed combustor per mole of SO_2 produced in the regenerator may range from about 20 to 100 depending mainly upon the amount of sulfur in the coal. Thus, as a minimum, the regenerator will consume from about one to four percent of the total power plant coal.

The corresponding maximum SO_2 mole fraction produced in the regenerator may be projected from

$$X_{SO_2} = \left[\frac{N_C}{N_{SO_2}} (3.762\ (1 + 1/4\alpha) + 1 + 1/2\alpha) - 1.881\ (1 + 4\ (N_{MeS}/N_{SO_2}) + 1 \right]^{-1}$$

Again, for $\alpha = 1.1$, $N_{MeS}/N_{SO_2} = 0$, and N_C/N_{SO_2} equal to the minimum value of 0.81, the maximum value for X_{SO_2} is 0.25, (not considering thermodynamics). Thus, material and energy balance limitations will control use of those sorbents having thermodynamic projections of X_{SO_2} greater than 0.25. If an ξ of 0.80 is required to supply the required regenerator energy, then the maximum SO_2 would be about 9.6 percent.

TWO-STEP REGENERATION SCHEMES

The metal sulfide formation step of the two-step regeneration processes is closely related to the reductive decomposition regeneration scheme. In situ partial combustion of coal produces reductant and energy under the proper conditions to promote the sulfide formation reaction. A material balance shows that

$$N_C/N_{H_2S} = \frac{2\ (N_{MeS}/N_{H_2S})}{(1 - \xi)\ (1 + 1/4\alpha)} ,$$

where N_{H_2S} is the number of moles of H_2S generated per unit time in the second step, H_2S generation, of the two-step process. The ratio N_{MeS}/N_{H_2S} may range between unity and Uc/(Uc - Ur) where Uc is the sorbent utilization in the combustor and Ur is the sorbent utilization in the regenerator. The minimum value of N_C/N_{H_2S}, based on an assumed minimum value of ξ of 0.5, $\alpha = 1.1$, and $N_{MeS}/N_{H_2S} = 1$, is 3.26. Thus, since the moles of carbon consumed in the fluid-bed combustor per mole of H_2S from the second-step regenerator may range from 20 to 100, the sulfide generation step will require a minimum of about 3 to 16 percent of the power plant fuel energy, depending upon the sulfur content of the coal.

The second step requires reaction of the metal sulfide with steam or with a steam/CO_2 mixture. Material and energy balances should not limit the formation of H_2S. The system will be either thermodynamically or kinetically limited, unless for some practical reason temperature control of the reaction cannot be achieved.

The molar rate of steam required for the reaction is related to the molar rate of H_2S production by

$$\frac{N_{H_2O}}{N_{H_2S}} = \frac{1}{X_{H_2S}}$$

for reaction with steam, and

$$\frac{N_{H_2O}}{N_{H_2S}} = \frac{R}{1 + R} \left(\frac{1}{X_{H_2S}} + 1\right)$$

for reaction with steam and CO_2, where N_{H_2O} is the number of moles of H_2O fed to the second-step regenerator. The factor R is equal to the ratio of steam to CO_2 in the reaction mixture. A value of 6 for N_{H_2O}/N_{H_2S} represents about one percent of the power plant fuel energy for a 4 weight percent sulfur coal. This corresponds to about 17 percent H_2S in the regenerator product gas for the steam reaction and about 9 percent H_2S for the steam/CO_2 reaction.

SUMMARY

Tables 18, 19, and 20 summarize the projections of sorbent performance taken from both the thermodynamic evaluations and the consideration of material and energy balances. Table 18 presents the results for the reductive decomposition scheme, Table 19 for the two-step process at atmospheric pressure, and Table 20 for the two-step process at 1000 kPa pressure.

The tables project regenerator temperature ranges, maximum SO_2 (or H_2S) mole fractions, and minimum carbon (or steam) consumption factors. For the reductive decomposition scheme, the minimum temperature limit is based on the equilibrium SO_2 mole percentage of 4 (the minimum acceptance

TABLE 18. RESULTS OF MATERIAL AND ENERGY BALANCE CONSIDERATIONS FOR REGENERATION BY REDUCTIVE DECOMPOSITION

Sorbent (Form stable in combustor)	AFBC (100 kPa)			PFBC (1000 kPa)		
	Regeneration Temperature Range, °C[a]	Maximum SO_2, %[b]	Minimum N_c/N_{SO_2}[c]	Regeneration Temperature Range, °C[a]	Maximum SO_2, %[b]	Minimum N_c/N_{SO_2}[c]
Na_2CO_3	740– 865	10	1.80	--	--	--
CaO	920–1150	25	0.81	1060–1150	16	1.18
$CaCO_3$	920–1150	25	0.81	1060–1150	16	1.18
$SrCO_3$	>1150	--	--	>1150	--	--
$LiAlO_2$	700– 860	25	0.81	850– 860	5	3.45
$LiFeO_2$	720– 860	25	0.81	820– 860	6	2.90
Li_2TiO_3	800– 860	9	1.98	--	--	--
$NaAlO_2$	590– 884	25	0.81	--	--	--
$NaCO_3 \cdot Fe_2O_3$	690– 856	10	1.80	--	--	--
$CaAl_2O_4$	740–1150	25	0.81	830–1150	25	0.81
$SrAl_2O_4$	760–1150	25	0.81	860–1150	25	0.81
$SrTiO_3$	580–1150	25	0.81	700–1150	25	0.81
$BaAl_2O_4$	710–1150	25	0.81	810–1150	25	0.81
$BaTiO_3$	720–1150	25	0.81	820–1150	25	0.81

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[a] Minimum temperature corresponds to SO_2 mole fraction of 0.04 based on thermodynamics; maximum temperature based on sorbent melting or coal-ash melting (assumed to be 1150°C), whichever is lower.

[b] Based on a minimum air/fuel ratio in the regenerator of 50% of stoichiometric or on thermodynamic limit, whichever is lowest.

[c] Represents the ratio of moles of carbon (in coal to the regenerator) to moles of SO_2 produced in the regeneration process based on material balance only. The corresponding value of this ratio in the combustor may range from 20 to 100.

TABLE 19. RESULTS OF MATERIAL AND ENERGY BALANCE CONSIDERATIONS FOR REGENERATION BY THE TWO-STEP PROCESS - AFBC

Sorbent (Form stable in combustor)	First-Step Temperature[a] Range, °C	Second Step with Steam			Second Step with Steam/CO_2		
		Temperature Range, °C[b]	Maximum H_2S, %[c]	Minimum N_{H_2O}/N_{H_2S}[d]	Temperature Range, °C[b]	Maximum H_2S, %[c]	Minimum N_{H_2O}/N_{H_2S}[d]
Na_2CO_3	400-550	—	—	—	300-856	99	1.01
CaO	400-680	—	—	—	300-500	18	3.28
$CaCO_3$	400-550	—	—	—	300-500	18	3.28
$SrCO_3$	400-750	—	—	—	300-720	39	1.78
$BaCO_3$	400-770	—	—	—	300-780	77	1.15
$LiAlO_2$	400-550	300-860	99	1.01	—	—	—
$LiFeO_2$	400-520	700-860	6	16.67	—	—	—
Li_2TiO_3	400-500	300-860	95	1.05	—	—	—
$NaAlO_2$	400-500	300-884	39	2.56	300-670	31	2.11
$Na_2CO_3 \cdot Fe_2O_3$	400-500	800-884	5	20.0	300-856	79	1.13
$CaAl_2O_4$	400-540	700-1300	9	11.11	300-630	57	1.38
$SrAl_2O_4$	400-550	300-1300	60	1.67	300-730	54	1.43
$SrTiO_3$	400-500	300-1300	99	1.01	—	—	—
$BaAl_2O_4$	400-550	300-1200	99	1.01	—	—	—
$BaTiO_3$	400-500	300-1300	99	1.01	—	—	—

[a] For first step minimum value of N_C/N_{H_2S} is 3.26 for all sorbents based on a minimum air/fuel ratio of 50% of stoichiometric. Minimum temperature based on estimate of minimum coal partial oxidation temperature; maximum temperature based on limiting SO_2 release to 10^{-2} mole % or sorbent melting.

[b] Minimum temperature based on avoiding steam condensation (300°C) or achieving minimum X_{H_2S} of 0.03; maximum temperature based on sorbent melting poing or achieving X_{H_2S} of 0.03.

[c] Based on thermodynamic equilibrium.

[d] Represents the moles of steam supplied to the reactor per mole of H_2S produced. For a 4 wt% sulfur coal a N_{H_2O}/N_{H_2S} ratio of 6 represents about 1% of the power plant fuel energy required for the second step.

TABLE 20. RESULTS OF MATERIAL AND ENERGY BALANCE CONSIDERATIONS FOR REGENERATION BY THE TWO-STEP PROCESS - PFBC

Sorbent (Form stable in combustor)	First-Step Temperature Range, °C[a]	Second Step with Steam			Second Step with Steam/CO_2		
		Temperature Range, °C[b]	Maximum H_2S, %[c]	Minimum N_{H_2O}/N_{H_2S}[d]	Temperature Range, °C[b]	Maximum H_2S, %[c]	Minimum N_{H_2O}/N_{H_2S}[d]
CaO	400-760	—	—	—	300-690	55	1.41
$CaCO_3$	400-760	—	—	—	300-690	55	1.41
$SrCO_3$	400-910	—	—	—	300-880	73	1.18
$BaCO_3$	400-1000	—	—	—	300-920	99	1.01
$LiAlO_2$	400-600	300-860	99	1.01	—	—	—
$LiFeO_2$	400-590	700-860	6	16.67	—	—	—
Li_2TiO_3	400-500	300-860	95	1.05	—	—	—
$CaAl_2O_4$	400-615	700-1300	9	11.11	300-700	83	1.10
$SrAl_2O_4$	400-625	300-1300	60	1.67	300-850	82	1.11
$SrTiO_3$	400-500	300-1300	99	1.01	—	—	—
$BaAl_2O_4$	400-580	300-1200	99	1.01	—	—	—
$BaTiO_3$	400-550	300-1300	99	1.01	—	—	—

[a] For first step minimum value of N_C/N_{H_2S} is 3.26 for all sorbents based on a minimum air/fuel ratio of 50% of stoichiometric. Minimum temperature based on estimate of minimum coal partial oxidation temperature; maximum temperature based on limiting SO_2 release to 10^{-2} mole % or sorbent melting.

[b] Minimum temperature based on avoiding steam condensation (300°C) or achieving minimum X_{H_2S} of 0.03; maximum temperature based on sorbent melting point or achieving X_{H_2S} of 0.03.

[c] Based on thermodynamic equilibrium.

[d] Represents the moles of steam supplied to the reactor per mole of H_2S produced. For a 4 wt% sulfur coal a N_{H_2O}/N_{H_2S} ratio of 6 represents about 1% of the power plant fuel energy required for the second step.

criterion), and the maximum temperature limit is based on melting-point limits or on the ash-softening point (assumed to be 1150°C). For the two-step regeneration processes the minimum temperature of the first step (sulfide production) is selected as the minimum to conduct in situ partial oxidation of coal (~400°C). The minimum temperature for the second-step reaction (300°C) is selected to avoid steam condensation. The maximum temperature limits are based on achieving the thermodynamic acceptance criteria or avoiding sorbent melts.

The maximum SO_2 or H_2S mole fractions are based on the lowest of the thermodynamic, the material, and the energy balance limits. While the carbon and steam consumptions are large for some of the sorbents, most of this energy should be recoverable through proper system design. The limiting factors will be capital investment and system complexity.

Some of the alternative sorbents are of limited potential, although they do satisfy the acceptance criteria. For example, $LiAlO_2$ and $LiFeO_2$ could produce only limited SO_2 concentrations by reductive decomposition at 1000 kPa pressure and are applicable over a very limited temperature range. Li_2TiO_3 also has a limited applicable temperature range for the atmospheric-pressure reductive decomposition.

The tabulated results provide an indication of the potential performance of the alternative sorbents. The results also identify the temperature ranges at which reaction kinetics should be investigated for the most promising alternative sorbents.

Some other factors should be considered when the results in Tables 18, 19, and 20 are used. First, the thermodynamics involved with many of the sorbents are speculative, and the original references should be reviewed to note their limitations. Secondly, the assessment has been consistently based on optimistic assumptions in order to project the maximum possible performance. For example, secondary reactions of several types could occur which could lead to deactivation of the sorbent or reduce the level of H_2S or SO_2 concentration in the regenerator product.

SECTION 8

AVAILABILITY

Availability data have been collected from standard references.[10-15] In general, sufficient commercial production of the simple metal oxides exists for their availability to be assessed, but the double oxides are available in such limited production that the availability of the raw materials required to produce them must be considered along with the feasibility of industrial expansion for their production. For example, in 1960 about 3,000 Mg of $BaTiO_3$ were produced at a cost of about $16,000/Mg and in 1957 about 12,000 Mg of $NaAlO_2$ were produced at about $250/Mg. Neither of these production rates would support a viable fluidized-bed combustion industry. The availability of sorbent support materials is also considered.

DATA

The basic raw materials required to produce all of the candidate sorbents are $BaCO_3$, $SrCO_3$, TiO_2, Fe_2O_3, Al_2O_3, Li_2CO_3, Na_2CO_3, and $CaCO_3$. The following summary sheets (Tables 21 through 28) of availability facts relate to these materials. Cost information is also included in the tables. The information in the tables does not provide a perspective until a specific model of the sorbent requirements is developed, but it is interesting to compare the annual production and US resources of coal to these sorbent materials. In 1973 about 600×10^6 Mg of coal were produced in the US, 65 percent of which was consumed by the electric utility industry, 15 percent for coke production, and 15 percent for industrial use. The identified coal resources in the US are about $1,600 \times 10^9$ Mg, and the ultimate reserves may be a factor of two larger. The sorbent resources are insignificant compared to those of coal (even for bauxite and iron ore), except for sodium carbonate

TABLE 21. $BaCO_3$ STATISTICS

Applicable Sorbents - $BaAl_2O_4$, $BaTiO_3$, $BaCO_3$
Commercial Mineral Forms
    Barite ($BaSO_4$)
    Witherite ($BaCO_3$) - almost entirely from England

Mineral Resources (identified)
    US - 99 million Mg (US is self-sufficient)
    World - 300 million Mg

Mineral Production (1975)
    US - 1.1 million Mg Barite
    Imports - 0.6 million Mg Barite

Distribution - Mined in eight states, 50% in Nevada; five firms produce 70% (poor distribution)

Commercial Uses - 80% in petroleum industry; remainder glass, paint, rubber, barium compounds

Price (fob mine, 1975) - $15.00/Mg (Barite)

Compounds
    $BaCO_3$ - production (1961) - 78,000 Mg; price (1972) - $150/Mg (chemical grade)
    $BaTiO_3$ - production (1960) - 3,000 Mg; price (1960) - $16,000/Mg

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TABLE 22. $SrCO_3$ STATISTICS

Applicable Sorbents - $SrCO_3$, $SrAL_2O_4$, $SrTiO_3$
Commercial Mineral Forms
- Celestite ($SrSO_4$)
- Strontianite ($SrCO_3$)

Mineral Resources (identified)
- US - 1 million Mg strontium - not economically recoverable
- World - very large, mainly celestite, Mexico and Canada chief suppliers

Mineral Production (1975)
- US - no domestic mining since 1959
- World - 36,600 Mg
- Imports - 22,000 Mg

Distribution - poor; 6 firms produce compounds in California, Georgia, New Jersey, Ohio
Commercial Uses - 48% for color T.V. tubes

Price (1975) - \$24/Mg of mineral, ∿\$50/Mg of Sr

Compounds
- $SrCO_3$ - production (1972) - 15,000 Mg; price (fob, 1970) - \$380/Mg (technical grade), \$700/Mg (pure)
- $SrSO_4$ - price (fob, 1970) - \$60/Mg
- $SrNO_3$ - price (fob, 1970) - \$240/Mg

TABLE 23. TiO_2 STATISTICS

Applicable Sorbents - Li_2TiO_3, $SrTiO_2$, $BaTiO_3$
Commercial Mineral Forms
    Rutile (TiO_2)
    Ilmenite ($FeTiO_3$) - 1.8-20% TiO_2
    Titanium slag

Mineral Resources (identified)
    US - 500,000 Mg Rutile - dependent on foreign supply
        100 million Mg Ilmenite
    World - 13.7 million Mg Rutile
        580 million Mg Ilmenite

Mineral Production (1975)
    US - 11,000 Mg rutile; 640,000 Mg ilmenite
    Imports - 216,000 Mg rutile; 450,000 Mg ilmenite

Distribution - rutile mined in Florida; 76% ilmenite mined in Florida and New York; six firms produce concentrates in New York, Florida, Georgia, and New Jersey

Commercial Uses - welding rod, pigment industries

Price (fob, 1975) - $710/Mg rutile, $55/Mg ilmenite

TABLE 24. Fe_2O_3 STATISTICS

Applicable Sorbents - $LiFeO_2$, $NaCO_3^* \cdot Fe_2O_3$

Commercial Mineral Forms
    Iron ore

Mineral Resources
    US - 4 billion Mg recoverable iron

Mineral Production (1975)
    US - 82 million Mg
    Imports - 47 million Mg

Price (fob, 1975) - $19.00/Mg natural ore

TABLE 25. Al_2O_3 STATISTICS

Applicable Sorbents - $LiAlO_2$, $NaAlO_2$, $CaAL_2O_4$, $SrAL_2O_4$, $BaAl_2O_4$, also support material

Commercial Mineral Forms
    Bauxite (35 - 65% Al_2O_3)

Mineral Resources (Bauxite)
    US - 40 million Mg (inadequate long term supply)
    World - 17 billion Mg

Mineral Production (Bauxite, 1975)
    US - about 2 million Mg - dependent on foreign supply
    Imports - about 12 million Mg

Distribution - Mined in Arkansas, Georgia, Alabama

Commercial Uses - 91% (1975) used to produce alumina; 88% of alumina used to produce aluminum; alumina used for adsorbents, catalysts, ceramics, abrasives, refractories; 0.15 million Mg (1963) of SiO_2-AL_2O_3 cracking catalyst produced

Price (Bauxite, fob mine, 1975) - $10-20/Mg

AL_2O_3 - production of all types (1975) - 0.2 million Mg; price (1972) - $120-300/Mg

TABLE 26. Li_2CO_3 STATISTICS

Applicable Sorbents - $LiAlO_2$, $LiFeO_2$, Li_2TiO_3
Commercial Mineral Forms
    Brine - as by-product
    Spodumene - 1-2% Li_2O ($LiAlSi_2O_6$)

Mineral Resources (reserves)
    US - 1.8 million Mg Li_2O - self-sufficient
    World - 2.9 million Mg Li_2O

Mineral Production
    Not available
    Exports (1975) - 800 Mg

Distribution - Mined and milled in N.C.; recovered from brines in Nevada

Commercial Uses - glass, ceramics, grease, air conditioning, storage batteries, metallurgy

Price (fob, 1975) - $130/Mg spodumene concentrate

Compounds - Li_2CO_3
    Consumption (1960) - 1,200 Mg; distribution - plants in PA. and TE.; capacity (1975) - 27,000 Mg/yr; Price (1975) - $1,600/Mg (chem. grade)

TABLE 27. Na_2CO_3 STATISTICS

Applicable Sorbents - Na_2CO_3, $NaAlO_2$, $NaCO_3 \cdot Fe_2O_3$
Commercial Mineral Forms
Natural soda ash
Salt cake (Na_2SO_4)
Sodium chloride (brine)

Mineral Resources
US - 50 million Mg soda ash (53-63% Na_2CO_3) >400 million Mg salt cake

Mineral Production (1975)
Natural soda ash - 4 million Mg
Salt cake - 665,000 Mg

Distribution - four natural soda ash producers in Wyoming and California; three natural salt cake producers in California, Texas, and Utah

Commercial Uses (Na_2CO_3) - 47% glass, 25% chemicals; pulp and paper

Price (fob, 1975) - \$54-64/Mg natural soda ash
- \$45/Mg salt cake

Compounds
Na_2CO_3 - 9 firms producing from natural soda or brine by Solvay process
$NaALO_2$ - production (1957) - 11,000 Mg; price (1957) - \$200-260/Mg

TABLE 28. $CaCO_3$ STATISTICS

Applicable Sorbents - $CaCO_3$, $CaAL_2O_4$
Commercial Mineral Forms
- Limestone - $CaCO_3$
- Dolomite - $CaCO_3 \cdot MgCO_3$
- Gypsum - $CaSO_4$

Mineral Resources
- Not estimated; projected to be sufficient for thousands of years at present consumption

Mineral Production (1972)
- >500 million Mg Limestone
- >60 million Mg dolomite

Distribution - resources in every state; widely distributed by many companies

Price (fob, 1975) - \$2-20/Mg limestone or dolomite and limestone/dolomite. Sodium carbonate represents about three percent of the resources of coal, and limestone apparently far exceeds coal resources. The annual production rates of all the sorbent materials except limestone are very small compared to those of coal; limestone rates are comparable.

The point of view developed for the availability and suitability of support materials for the production of alternative sorbents is that: (1) there are a number of ceramic raw materials occurring in nature (clays, silicas, feldspar, etc.) that would not be expected to be suitable support materials because of their limited availability and poor attrition resistance; (2) the only support material that may possibly have sufficient availability and attrition resistance would be a specially prepared alumina structure.

SORBENT DEMAND MODEL

The demand for a sorbent material may be projected from the relationship

$$M = \varepsilon M_o C_o [(1.05)^n - 1] [f + 0.0476] \quad ,$$

where M is the annual mass of sorbent required in a year n years after 1990, ε is the fraction of the new coal-fired power generation market captured by fluidized-bed combustion annually, M_o is the initial mass of sorbent required for a new fluid-bed combustion plant (Mg per MWe), C_o is the US power demand (electric utility coal-fired) in the year 1990, the year in which fluidized-bed combustion is assumed to become a viable commercial industry, and f is the fraction of the initial plant sorbent that must be replaced annually in order to make up for losses due to attrition, deactivation, elutriation, agglomeration and handling, and so on. The factor $(1.05)^n$ accounts for an assumed 5 percent growth in power generation demand per year. The term M_o is a function of the plant design, the sorbent density, and the fraction of support material comprising the total sorbent structure.

In order to project the sorbent demand, or to project acceptable rates of loss of the alternative sorbents due to all causes, the following assumptions are made:

- The sorbent structure consists of 30 weight percent active sorbent and 70 weight percent alumina support;
- The combustor volume is identical to the volume for the limestone/dolomite combustor at about 1060 dm^3 (30,000 ft^3) per 1000 MWe power plant for all of the sorbents.
- The coal-fired capacity in 1990 is 5×10^5 MWe (C_o), and fluid-bed combustion captures 25 percent of the new market annually (ε).

The results in Table 29 are obtained with these assumptions. The sorbent loss rate is expressed as a percentage of the bed inventory lost per hour (a function of f), which leads to a sorbent demand, M (of the limiting component) in the year 2000 (10 years after the assumed commercial start) equivalent to the 1975 production level. The selection of the year 2000 and the production level in 1975 are arbitrary, but the results do provide a perspective on the tolerable loss rates. For comparison, the normal attrition rate for limestone and dolomite in a fluid-bed combustor is on the order of 1 percent per hour, while total deactivation plus attrition losses are about 10 percent per hour.

The analysis does not provide a clear breakpoint in the loss rate of sorbent that separates acceptable from unacceptable behavior, but it is evident that a great increase in demand for any material, such as is expressed in Table 29, would require a large obligation by industry to expand and invest capital. Certainly,an alternative sorbent should not be developed if it cannot support an industry. The sorbents other than Na_2CO_3, $CaO/CaCO_3$, $NaAlO_2$, $NaCO_3 \cdot Fe_2O_3$, and $CaAl_2O_4$ appear to require extremely low loss rates when all of the possible sources for sorbent losses are considered: combustor and regenerator attrition; cyclone attrition; pneumatic transport attrition; deactivation due to sintering and poisoning; and handling, maintenance,and preparation losses.

TABLE 29. SORBENT AVAILABILITY COMPARISON

Sorbent[a] (Form Stable in Combustor)	Limiting Component	Percent of the Combustor Inventory Lost per Hour (in 2000) to Equal the 1975 US Production Rate of Limiting Component[b,c]
Na_2CO_3	Al_2O_3	3.64
$CaO/CaCO_3$	Al_2O_3	2.77
$SrCO_3$	$SrCO_3$	0.011
$BaCO_3$	$BaCO_3$	0.054
$LiAlO_2$	Li_2CO_3	0.044
$LiFeO_2$	Li_2CO_3	0.113
Li_2TiO_3	Li_2CO_3	0.033
$NaAlO_2$	Al_2O_3	2.41
$NaCO_3 \cdot Fe_2O_3$	Al_2O_3	3.07
$CaAl_2O_4$	Al_2O_3	1.94
$SrAl_2O_4$	$SrCO_3$	0.015
$SrTiO_3$	$SrCO_3$	0.010
$BaAl_2O_4$	$BaCO_3$	0.070
$BaTiO_3$	$BaCO_3$	0.064

[a] Based on 30 wt% sorbent in an alumina support

[b] Based on the following assumptions: (1) Fluid-bed combustion commercial in 1990; (2) Coal-fired electric utility generation of 2×10^5 MWe in 1990; (3) 5% annual increase in coal-fired power generation; (4) fluid-bed combustion captures 25% of the new coal-fired power generation capacity.

[c] See Tables 21-28 for US and world 1975 resource estimates.

Even the projections for the five sorbents that have apparently high availability may be overly optimistic. The limiting component for each of these sorbents is the alumina support material. Table 29 is based on all forms of alumina currently produced; but (from Table 25) 88 percent of this current production is presently utilized in the production of aluminum. Thus, the increase in alumina production for the catalyst-type uses assumed here would be in reality much larger, or the tolerable loss rate should be smaller by a large factor (about 10).

SECTION 9

ECONOMICS

Ultimately, the alternative sorbent must provide an economic advantage over the limestone/dolomite-based fluidized-bed combustion system to be considered for development. The total cost of the sorbent consists of contributions from the sorbent material (and support) cost and the capital investment associated with the power plant, both of which are influenced by the sorbent behavior. Both of these contributions can be estimated, and the tolerable rate of sorbent losses can be projected.

SORBENT MATERIAL COST

The cost associated with the direct consumption of the sorbent consists of the raw materials cost, the delivery cost of the raw materials and the cost of preparation of the sorbent particles. The delivery cost of some of the raw materials could be high because of the poor distribution of producers in the country. Preparation could also be very expensive. Various preparation techniques could be used. For example, the raw materials could be transformed first into the desired metal oxide form, and then the metal oxide could be fixed to the support structure by slurrying or impregnation, followed by drying and sizing of the sorbent material. It is assumed that a separate industry would be initiated to supply the sorbent needs of the utilities rather than on-site preparation of the sorbent.

The costs of the sorbent raw materials are estimated in Table 30 for an alumina support costing $200/Mg and for the sorbent particles containing 30 weight percent sorbent material. Availability limitations are neglected, and present day sorbent material costs are assumed; increased demand would increase these costs. A minor factor has been included

TABLE 30. SORBENT RAW MATERIALS COSTS

Sorbent	Components (Cost \$/Mg)	Sorbent Raw Materials Cost (\$/Mg)[a]
Na_2CO_3	Na_2CO_3 (85)	166
$CaO/CaCO_3$	$CaCO_3$ (10)	143
$SrCO_3$	$SrCO_3$ (450)	275
$BaCO_3$	$BaCO_3$ (180)	194
$LiAlO_2$	Li_2CO_3 (1,800), Al_2O_3 (200)	489
$LiFeO_2$	Li_2CO_3 (1,800), Fe_2O_3 (67)	270
Li_2TiO_3	Li_2CO_3 (1,800), TiO_2 (800)	678
$NaAlO_2$	Na_2CO_3 (85), Al_2O_3 (200)	194
$Na_2CO_3 \cdot Fe_2O_3$	Na_2CO_3 (85), Fe_2O_3 (67)	159
$CaAl_2O_4$	$CaCO_3$ (10), Al_2O_3 (200)	181
$SrAl_2O_4$	$SrCO_3$ (450), Al_2O_3 (200)	267
$SrTiO_3$	$SrCO_3$ (450), TiO_2 (800)	353
$BaAl_2O_4$	$BaCO_3$ (180), Al_2O_3 (200)	206
$BaTiO_3$	$BaCO_3$ (180), TiO_2 (800)	268

[a] Cost per Mg of sorbent plus support based on 30 wt% sorbent in an alumina support. The support alumina material is assumed to cost \$200/Mg. Does not include raw material losses during preparation and handling; 1975 cost basis; assumes delivery cost, is minimal.

for delivery but is not expected to be representative of actual delivery costs except under ideal conditions. Preparation costs may range up to $2000/Mg, but because there is presently no basis for predicting the preparation cost, its influence will be observed parametrically.

MAXIMUM ACCEPTABLE TOTAL SORBENT COST

It is assumed that the total cost of power from the fluidized-bed combustion power plant with an alternative sorbent must not exceed the cost of power from the limestone/dolomite-based power plant. The limestone/dolomite-based system could utilize either the once-through sorbent concept or the reductive decomposition regeneration concept. Economic comparison will be made for both of these concepts. The maximum acceptable sorbent cost will be calculated in order to be competative with limestone/dolomite-based sorbents, and this cost will be translated into a maximum acceptable sorbent loss rate due to attrition, deactivation, and so on.

An alternative sorbent may influence the design and cost of many components in the power plant (e.g., sorbent storage, feeding, combustor design, power generation equipment, particulate control, etc.), but for this analysis it is assumed that all plant components are identical in cost when comparing the alternative sorbents with the limestone/dolomite sorbent, except for the cost of the regeneration system. The regeneration system consists of the regenerator components, the sorbent circulation components, the sulfur recovery process, the CO_2 recovery process (if applicable), and required auxiliary components. Spent sorbent processing equipment is not included. Thus, the following discussion will consider only those components of the total plant.

The maximum performance in terms of SO_2 or H_2S mole fractions from the regenerator have been projected in Tables 18, 19, and 20. Because this is the most critical cost-determining factor in the regenerator system, the capital cost corresponding to this maximum performance represents the minimum possible investment. The capital investment for sulfur recovery processes as a function of the fraction SO_2 or

H_2S has been estimated. Previous cost assessments of regeneration indicate that the total capital investment for regeneration may be related directly to the sulfur recovery investment. It is assumed that the total regeneration system investment is equal to 1.47 times the sulfur recovery investment for the reductive decomposition regeneration and 2.0 times the sulfur recovery investment, plus the CO_2 recovery system investment for the two-step regeneration processes.

For the comparison it is assumed that the limestone/dolomite-based reductive decomposition regeneration system investment is $29/kW for the atmospheric-pressure system and $61/kW for the pressurized system (based on a 600 MWe power plant). The base limestone/dolomite reductive decomposition regeneration energy costs are estimated to be 2.55 mills/kWh for the atmospheric-pressure system and 4.00 mills/kWh for the pressurized system. The limestone/dolomite-based once-through energy cost is assumed to be 2.0 mills/kWh for the atmospheric-pressure system (based on a calcium-(limestone)/sulfur mole ratio of 3) and 1.3 mills/kWh for the pressurized system (based on a calcium (dolomite)/sulfur mole ratio of 1.2).

The energy cost associated with the regeneration system consists of contributions from five factors: capitalization of the investment, operating and maintenance cost, fuel cost, power plus other auxiliary items, and the sorbent cost. Based on a 20 percent capitalization plus operating and maintenance factor, a 70 percent plant capacity factor, a 600 MWe power plant producing 200 Mg of sulfur per day and a coal cost of $20/Mg, the following energy cost relationship is developed for the reductive decomposition regeneration:

Minimum Energy Cost (mills/kWh)

$$= 0.0326\ (I) + (N_C/N_{SO_2})\ 0.1225 + 0.4 + S\quad ,$$

where I is the minimum regeneration system capital investment in $/kW, N_C/N_{SO_2} is the minimum coal rate factor in Table 18, and S is the sorbent cost in mills/kWh (sorbent price times sorbent consumption rate).

For the two-step regeneration processes

Minimum Energy Cost (mills/kWh)

$$= 0.0326\ (I) + (N_{H_2O}/N_{H_2S})\ 0.0174 + 0.8 + S\quad ,$$

where N_{H_2O}/N_{H_2S} is the steam consumption factor in Tables 19 and 20.

Applying all of the assumptions stated provides a means to estimate the maximum acceptable sorbent cost (S) for comparison with either the regenerative base system or the once-through base system. The results from this comparison are presented in Tables 31, 32, and 33 for the reductive decomposition and the two-step regeneration processes. Relative conclusions may be drawn from the three tables. The results indicate that there is very little economic incentive to develop alternative sorbents for pressurized fluidized-bed combustion if the basis of comparison is the pressurized calcium-based once-through performance (i.e., the maximum permissible alternative sorbent costs in column four of Tables 31, 32, and 33 are near zero or, in some cases, less than zero. On the other hand, the economic incentive to develop alternative sorbents is highest for the pressurized systems if the basis of comparison is the pressurized calcium-based regeneration performance (i.e., the permissible sorbent costs are the greatest in column three of Table 31 and columns 1 and 2 of Table 33). The economic incentive to develop alternative sorbents for the atmospheric-pressure system is lower than for the pressurized system, comparing columns 1 and 3 in Table 31 (i.e., because more expensive sorbent materials may be used in the pressurized systems than in the atmospheric-pressure systems, more opportunity for economic advantage is available in the pressurized regeneration systems).

TABLE 31. MAXIMUM ACCEPTABLE ALTERNATIVE SORBENT COST FOR REDUCTIVE DECOMPOSITION REGENERATION(S), mills kWh[a]

	AFBC		PFBC	
	Comparison with		Comparison with	
Sorbent	Base Regeneration[b]	Base Once-through[c]	Base Regeneration[d]	Base Once-through[e]
Na_2CO_3	0.98	0.43	--	—
$CaO/CaCO_3$	1.43	0.88	2.71	0.01
$SrCO_3$	1.43	0.88	--	—
$LiAlO_2$	1.43	0.88	1.68	<0
$LiFeO_2$	1.43	0.88	1.88	<0
Li_2TiO_3	0.83	0.28	--	—
$NaAlO_2$	1.43	0.88	--	—
$NaCO_3 \cdot Fe_2O_3$	0.98	0.43	--	—
$CaAl_2O_4$	1.43	0.88	2.88	0.18
$SrAl_2O_4$	1.43	0.88	2.88	0.18
$SrTiO_3$	1.43	0.88	2.88	0.18
$BaAl_2O_4$	1.43	0.88	2.88	0.18
$BaTiO_3$	1.43	0.88	2.88	0.18

[a] The figures given in the table are the alternative sorbent cost, S (expressed in mills/kWh) which would be necessary for the alternative sorbent reductive decomposition regeneration system to have a cost equal to that of the base limestone/dolomite regeneration and once-through cases indicated. S could be expressed as a product of the sorbent cost in \$/Mg and the sorbent consumption rate in Mg/kWh.

[b] Base regeneration is atmospheric pressure limestone/dolomite reductive decomposition.

[c] Base once-through is an atmospheric pressure limestone/dolomite once-through system.

[d] Base regeneration is a pressurized limestone/dolomite reductive decomposition.

[e] Base once-through is a pressurized limestone/dolomite once-through system.

TABLE 32. MAXIMUM ACCEPTABLE ALTERNATIVE SORBENT COST FOR
TWO-STEP ATMOSPHERIC-PRESSURE
REGENERATION(S), mills/kWh[a]

Sorbent	Two-Step Regeneration AFBC			
	With Steam		With Steam/CO_2	
	Comparison with		Comparison with	
	Base Regeneration[b]	Base Once-through[c]	Base Regeneration[b]	Base Once-through[c]
Na_2CO_3	--	--	0.85	0.30
$CaO/CaCO_3$	--	--	0.62	0.07
$SrCO_3$	--	--	0.68	0.13
$BaCO_3$	--	--	0.75	0.20
$LiAlO_2$	1.31	0.76	--	--
$LiFeO_2$	0.45	<0	--	--
Li_2TiO_3	1.21	0.66	--	--
$NaAlO_2$	1.12	0.57	0.68	0.13
$NaCO_3 \cdot Fe_2O_3$	0.23	<0	0.75	0.20
$CaAl_2O_4$	0.81	0.26	0.75	0.20
$SrAl_2O_4$	1.17	0.62	0.75	0.20
$SrTiO_3$	1.31	0.76	--	--
$BaAl_2O_4$	1.31	0.76	--	--
$BaTiO_3$	1.31	0.76	--	--

[a] The figures given in the table are the alternative sorbent cost, S (expressed in mills/kWh), regeneration schemes at atmospheric pressure to have the same energy cost as the base limestone/dolomite regeneration and once-through cases indicated.

[b] Base regeneration is atmospheric-pressure limestone/dolomite reductive decomposition.

[c] Base once-through is a atmospheric-pressure limestone/dolomite once-through system.

TABLE 33. MAXIMUM ACCEPTABLE ALTERNATIVE SORBENT COST FOR TWO-STEP PRESSURIZED REGENERATION (S), mills kWh[a]

	Two-Step Regeneration PFBC			
	With Steam		With Steam/CO_2	
Sorbent	Base Regeneration[b]	Base Once-through[c]	Base Regeneration[b]	Base Once-through[c]
Na_2CO_3	—	—	—	—
$CaO/CaCO_3$	—	—	2.20	<0
$SrCO_3$	—	—	2.20	<0
$BaCO_3$	—	—	2.30	<0
$LiAlO_2$	2.76	0.06	—	—
$LiFeO_2$	1.90	<0	—	—
Li_2TiO_3	2.73	0.03	—	—
$NaAlO_2$	—	—	—	—
$Na_2CO_3 \cdot Fe_2O_3$	—	—	—	—
$CaAl_2O_4$	2.26	<0	2.30	<0
$SrAl_2O_4$	2.57	<0	2.30	<0
$SrTiO_3$	2.76	0.06	—	—
$BaAl_2O_4$	2.76	0.06	—	—
$BaTiO_3$	2.76	0.06	—	—

[a] Base regeneration is pressurized reductive decomposition.

[b] Base once-through is a pressurized once-through system.

[c] The figures given in the table are the alternative sorbent cost, S (expressed in mills/kWh), which would be necessary for the alternative sorbent two-step regeneration schemes at pressure to regeneration and once-through cases indicated.

MAXIMUM ACCEPTABLE SORBENT LOSS RATE

The estimates of maximum acceptable sorbent cost given in Tables 31, 32, and 33 may be translated into maximum acceptable sorbent loss rates as a function of the sorbent preparation cost. The following relationship applies:

$$X = \left[\left(\frac{S}{C_M + C_p}\right) \frac{0.3 + \rho_s/2.8}{\rho_s \times 10^{-3}} - 0.143\right] 0.0163$$

where X is the maximum acceptable percentage of the combustor inventory lost per hour; S is the maximum acceptable sorbent cost in Tables 31, 32, and 33; C_M is the sorbent raw material cost estimated in Table 30; C_p is the sorbent preparation cost in \$/Mg; ρ_s is the sorbent material density; and ρ_c is the support material density. It is assumed in this relationship that the sorbent structure is comprised of 30 weight percent sorbent and 70 percent support, the particle is 50 percent void, the bed is 50 percent void, the support material density is about 4 g/cc (250 lb/ft^3), the bed volume is 1060 dm^3 (30,000 ft^3) per 1000 MWe plant, the capitalization factor on the original sorbent purchase is 0.1, and a 0.7 plant capacity factor is in effect.

Evaluation of the cost relationship for the value of S given in Tables 31, 32, and 33 under the calcium-based reductive decomposition regeneration base case results in the maximum loss rates reported in Tables 34, 35, and 36. Loss rates have not been determined on the basis of comparison with the once-through limestone/dolomite system because in most cases the resulting loss rates would be inconceivably small (<0.01 % per hour). The tables state that if (1) the sorbent performs at its maximum possible level of performance and (2) if the availability of the sorbent is not limiting so that the present sorbent costs may be assumed, then the rate of loss in the tables for a given sorbent preparation cost will result in an energy cost for the power plant identical with the limestone/dolomite-based power plant.

TABLE 34. MAXIMUM SORBENT LOSS RATES FOR REDUCTIVE DECOMPOSITION REGENERATION

		Maximum Acceptable Percentage of Combustor Bed Loss Per Hour[a]		
		Sorbent Preparation Cost, $/Mg		
Sorbent	System	0	500	1000
Na_2CO_3	AFBC	0.804	0.199	0.113
$CaO/CaCO_3$	AFBC	1.234	0.272	0.152
	PFBC	2.339	0.515	0.287
$SrCO_3$	AFBC	0.618	0.218	0.132
$LiAlO_2$	AFBC	0.372	0.183	0.121
	PFBC	0.437	0.215	0.142
$LiFeO_2$	AFBC	0.856	0.235	0.142
	PFBC	1.125	0.308	0.186
Li_2TiO_3	AFBC	0.148	0.085	0.057
$NaAlO_2$	AFBC	0.941	0.261	0.152
$NaCO_3 \cdot Fe_2O_3$	AFBC	0.787	0.187	0.106
$CaAl_2O_4$	AFBC	0.941	0.248	0.142
	PFBC	1.894	0.499	0.285
$SrAl_2O_4$	AFBC	0.637	0.220	0.132
	PFBC	1.283	0.443	0.266
$SrTiO_3$	AFBC	0.442	0.181	0.114
	PFBC	0.890	0.365	0.230
$BaAl_2O_4$	AFBC	0.807	0.233	0.135
	PFBC	1.625	0.469	0.272
$BaTiO_3$	AFBC	0.619	0.215	0.129
	PFBC	1.247	0.434	0.259

[a] Based on sorbent raw materials costs in Table 30 and the maximum acceptable sorbent costs in Table 31 using the columns reflecting the base regeneration system comparison.

TABLE 35. MAXIMUM SORBENT LOSS RATES FOR TWO-STEP REGENERATIONS AFBC

Sorbent	Regeneration Reactant Gas	Maximum Acceptable Percentage of Combustor Bed Loss Per Hour[a]		
		Sorbent Preparation Cost, $/Mg		
		0	500	1000
Na_2CO_3	H_2O/CO_2	0.698	0.173	0.098
$CaO/CaCO_3$	H_2O/CO_2	0.535	0.117	0.065
$SrCO_3$	H_2O/CO_2	0.293	0.104	0.064
$BaCO_3$	H_2O/CO_2	0.424	0.122	0.072
$LiAlO_2$	H_2O	0.341	0.168	0.111
$LiFeO_2$	H_2O	0.269	0.073	0.044
Li_2TiO_3	H_2O	0.217	0.124	0.086
$NaAlO_2$	H_2O	0.737	0.204	0.119
	H_2O/CO_2	0.447	0.124	0.072
$NaCO_3 \cdot Fe_2O_3$	H_2O	0.184	0.044	0.024
	H_2O/CO_2	0.603	0.143	0.082
$CaAl_2O_4$	H_2O	0.533	0.140	0.080
	H_2O/CO_2	0.494	0.130	0.075
$SrAl_2O_4$	H_2O	0.522	0.179	0.108
	H_2O/CO_2	0.334	0.116	0.068
$SrTiO_3$	H_2O	0.404	0.166	0.104
$BaAl_2O_4$	H_2O	0.738	0.214	0.117
$BaTiO_3$	H_2O	0.567	0.197	0.117

[a] Based on sorbent raw material costs in Table 30 and the maximum acceptable sorbent costs in Table 32 using the columns reflecting the base regeneration system comparison.

TABLE 36. MAXIMUM SORBENT LOSS RATES FOR TWO-STEP REGENERATIONS PFBC

Sorbent	Regeneration Reactant Gas	Maximum Acceptable Percentage of of Combustor Bed Loss per Hour[a] Sorbent Preparation Cost, \$/Mg 0	500	1000
$CaO/CaCO_3$	H_2O/CO_2	1.900	0.419	0.233
$SrCO_3$	H_2O/CO_2	0.950	0.336	0.204
$BaCO_3$	H_2O/CO_2	1.299	0.375	0.220
$LiAlO_2$	H_2O	0.717	0.352	0.233
$LiFeO_2$	H_2O	1.138	0.311	0.189
Li_2TiO_3	H_2O	0.487	0.279	0.192
$CaAl_2O_4$	H_2O	1.487	0.391	0.223
	H_2O/CO_2	1.513	0.398	0.228
$SrAl_2O_4$	H_2O	1.146	0.396	0.238
	H_2O/CO_2	1.025	0.354	0.212
$SrTiO_3$	H_2O	0.853	0.349	0.220
$BaAl_2O_4$	H_2O	1.557	0.450	0.261
$BaTiO_3$	H_2O	1.195	0.416	0.248

[a] Based on sorbent raw materials costs in Table 30 and the maximum acceptable sorbent costs in Table 33, using the columns reflecting the base regeneration system comparison.

If the sorbents performed at their maximum level and cost nothing to prepare, some of them could operate with maximum loss rates similar to the attrition loss rates of limestones and dolomites (1 to 5 percent per hour). Total sorbent loss rates for regenerative limestone/dolomite systems due to attrition, deactivation, and so forth, will be about 10 percent per hour or greater. With expected preparation costs and system performance, however, it would be expected that the loss rates must be at least an order of magnitude less than the loss rates of limestone and dolomite due to attrition alone in order to be economically competitive and even lower to provide sufficient economic incentive to develop the alternative sorbent. Experimentation will be required to demonstrate such low loss rates. Again, the pressurized systems appear to provide the greatest opportunity for an alternative sorbent.

If the comparison with the base once-through system had been made from Tables 31, 32, and 33, it is doubtful that any alternative sorbent could compete economically with the limestone/dolomite-based once-through system unless environmental constraints on spent sorbent place additional economic requirements on the once-through systems.

The projections presented in the tables not only provide a perspective or the sorbent loss requirements but also can act as a guide to experimental attrition/deactivation studies and show the relative potential of the candidate sorbents.

SECTION 10

ASSESSMENT OF ALTERNATIVE SORBENTS

Fourteen alternative sorbents have been identified in Table 18 as possibly being suitable for atmospheric-pressure fluidized-bed combustion: Na_2CO_3, $CaO/CaCO_3$, $SrCO_3$, $BaCO_3$, $LiAlO_2$, $LiFeO_2$, Li_2TiO_3, $NaAlO_2$, $NaCO_3 \cdot Fe_2O_3$, $CaAl_2O_4$, $SrAl_2O_4$, $SrTiO_3$, $BaAl_2O_4$ and $BaTiO_3$. These sorbents are reported in the form thermodynamically stable under the combustor conditions. Eleven sorbents are possibly suitable for pressurized fluidized-bed combustion (Tables 19 and 20): $CaO/CaCO_3$, Sr_2CO_3, $BaCO_3$, $LiAlO_2$, $LiFeO_2$, Li_2TiO_3, $CaAl_2O_4$, $SrAl_2O_4$, $SrTiO_3$, $BaAl_2O_4$ and $BaTiO_3$. Suitable regeneration processes for each of these sorbents have been identified and applicable temperature ranges and maximum performance levels have been projected.

Because sorbent losses by attrition and deactivation at a number of process locations are always to be expected, it appears that the availability of the active sorbent material or the support material will be the most important factor in justifying the development of fluidized-bed combustion with alternative sorbents. None of the alternative sorbent materials can compare with limestone/dolomite in availability and wide distribution of producers.

If maximum performance levels could be achieved, it is expected that sorbent loss rates must be less than 0.1 percent of bed content per hour in order to compete economically with limestone/dolomite-based fluidized-bed combustion (reductive decomposition regeneration). The availability limitations on the alternative sorbents may be more stringent than the economic.

Further development is required in attrition behavior, kinetics, and engineering studies concerning sorbent preparation costs, sorbent availability, the impact of design modifications that reduce attrition upon fluidized-bed combustion economics, and the environmental impact of alternative sorbents.

Attrition behavior under simulated process conditions should be characterized in order to select promising support materials, although availability may determine the support material and the preparation of the sorbent may become the issue.

The kinetics of desulfurization and regeneration should be characterized within the applicable range of operating conditions (temperature, pressure, fuel, etc.) and under conditions which simulate the maximum performance levels. Unless the high levels of SO_2 or H_2S can be achieved in the regeneration process, the alternative sorbents will become economically unfeasible. The degree of sorbent utilization and regeneration appears to be a relatively unimportant economic factor.

At present, too little is known about the cost of sorbent preparation. Feasible process technology for sorbent preparation should be proposed and the economic feasibility assessed.

The availability of the sorbent materials and the support materials may require more modeling in order to assess all of the market factors properly. The area of industrial expansion into alternative sorbent preparation and distribution must also be explored.

Alternative sorbents may require alternative fluidized-bed combustion design concepts to satisfy their limitations and promote their advantages. The impact of alternative designs that would reduce sorbent attrition/deactivation should be evaluated.

Finally, the environmental impact of alternative sorbents (e.g., trace metals released to the environment during combustion/regeneration, or upon disposal of deactivated sorbent) may lead to elimination of certain candidate materials. The complex sociological interactions of these materials must be explored before development is committed.

SECTION 11

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APPENDIX A

PROGRAM PLAN

Preliminary screening of alternative sorbents for fluidized-bed combustion has identified 14 candidates. Rather than attempt to evaluate all of these sorbents within the limited resources of the program, three of the most promising materials will be evaluated experimentally and economically.

The following tasks will be performed with the selected sorbents:

1. Evaluation of availability, cost, and properties of selected sorbents and support materials through contacts with industrial suppliers.
2. Evaluation of alternative sorbent commercial preparation methods and preparation costs.
3. Preparation of the selected sorbents, using commercial preparation techniques, and evaluation of the prepared sorbent physical and chemical properties.
4. Collection of data on desulfurization kinetics and regeneration kinetics under high-performance conditions. Testing of sorbent attrition at process conditions.
5. Assessment of plant performance and cost with the selected sorbents.
6. Proposal of development plan for the best alternative sorbent if it is commercially advantageous compared to the naturally occurring calcium-based sorbent materials.

SELECTION OF SUPPORT MATERIAL

On the basis of availability considerations the support material will be alumina. The prepared alumina properties to be utilized must provide a tradeoff between low cost, high attrition resistance, high sorbent kinetics promoted by large pore diameters and the amount of active sorbent that can be loaded. Alumina suppliers will be contacted.

SELECTION OF SORBENT MATERIALS

The 14 sorbents from which three materials have been selected are: Na_2CO_3, CaO, $SrCO_3$, $BaCO_3$, $LiAlO_2$, $LiFeO_2$, Li_2TiO_3, $NaAlO_2$, $NaCO_3 \cdot Fe_2O_3$, $CaAl_2O_4$, $SrAl_2O_4$, $SrTiO_3$, $BaAl_2O_4$ and $BaTiO_3$. The following table (Table A1) summarizes the technical potential, the cost and availability potential and the selection logic for these materials. The evaluation of the three selected alternative sorbents $BaCO_3$, $CaAl_2O_4$ and $BaTiO_3$, will provide information about other sorbent materials by induction.

SORBENT TESTING

Three critical test areas will be considered: attrition testing, desulfurization kinetics, and regeneration kinetics. The following general description of these tests provides an indication of their scope.

Attrition Tests

- Basic parameters. Temperature, pressure, velocity, gaseous environment, number of regeneration cycles, sorbent material structure, and sorbent preparation technique.
- Description. Samples will be fluidized under desulfurizer conditions and rates of fines generation will be measured. Both fresh and cycled samples will be tested.
- Criteria. Observed loss rates must be less than the economic limits previously determined for each sorbent.

Desulfurization Tests

- Basic parameters. Temperature, pressure, gaseous environment, number of cycles, sorbent composition, support structure, and particle size.

TABLE A1. ALTERNATIVE SORBENT SELECTION

Sorbent	Desulfurizer Potential		Reductive Decomposition Potential		2-Step Regeneration Potential		Availability Potential	Cost Potential	Selection Logic
	Atmospheric	Pressurized	Atmospheric	Pressurized	Atmospheric	Pressurized			
Na_2CO_3	Limited temp. range	No	Limited SO_2	No	Good	No	Good	—	Drop - Limited applicability; highly corrosive nature
CaO	Good	Good	Good	Limited SO_2	Limited H_2S	Good	Good	Good	Drop - Good potential, but similarity with $CaAl_2O_4$; existing data from Argonne
$SrCO_3$	Good	Good	No	No	Good	Good	Poor	—	Drop - Poor availability
$BaCO_3$	Good	Good	No	No	Good	Good	—	—	Select - Reasonable potential
$LiAlO_2$	Good	Good	Good	Limited SO_2	Good	Good	—	Poor	Drop - Poor cost potential
$LiFeO_2$	Good	Good	Good	Limited SO_2	Limited H_2S	Limited H_2S	—	Poor	Drop - Poor cost potential due to limited performance
Li_2TiO_3	Good	Good	Limited SO_2	No	Good	Good	—	Poor	Drop - Poor cost potential
$NaAlO_2$	Limited temp. range	No	Good	No	Good	No	Good	—	Drop - Limited applicability; highly corrosive nature
$NaCO_3 \cdot Fe_2O_3$	Limited temp. range	No	Limited SO_2	No	Good	No	Good	—	Drop - Limited applicability; highly corrosive nature
$CaAl_2O_4$	Good	Good	Good	Good	Good	Good	Good	Good	Select - Reasonable potential
$SrAl_2O_4$	Good	Good	Good	Good	Good	Good	Poor	—	Drop - Poor availability
$SrTiO_3$	Good	Good	Good	Good	Good	Good	Poor	—	Drop - Poor availability
$BaAl_2O_4$	Good	Good	Good	Good	Good	Good	—	—	Drop - Reasonable potential, but similarity with $BaCO_3$
$BaTiO_3$	Good	Good	Good	Good	Good	Good	—	—	Select - Reasonable potential

- Description. Sorbent desulfurization kinetics will be determined on TGA for fresh and cycled material, up to 20 cycles (if fresh material meets criteria). High performance conditions will be utilized (low SO_2 approaching the required level).
- Criteria. Kinetics should be within the same order of magnitude as the kinetics of limestone/dolomite sorbents. Deactivation on cycling must be limited to levels less than permissible sorbent attrition loss rates.

Regeneration Tests

- Basic parameters. Reaction scheme (reductive decomposition, two-step process with steam or steam and CO_2), temperature, pressure, gaseous environment, number of cycles, sorbent composition, support structure, and particle size.
- Description. Sorbent regeneration kinetics will be determined on TGA for fresh and cycled material (if fresh material meets criteria). High performance conditions will be utilized (high SO_2 or H_2S).
- Criteria. Kinetics should be within the same order of magnitude as the kinetics of limestone/dolomite sorbents. No criterion has been developed for the extent of sorbent regeneration (change in utilization).

Specific sorbent test conditions for $BaCO_3$, $CaAl_2O_4$, and $BaTiO_3$ are listed in Tables A2, A3, and A4. The program testing logic will be a set of specific tests arranged in series with a decision to halt testing or continue testing following each test step. This will minimize the number of tests required and will force an assessment of each test result to be performed.

This program will require between 1 and 1.5 years to complete, based on the present resources available.

TABLE A2. $BaCO_3$ TEST CONDITIONS

Particle size - <2000 µm; fines less than 100 µm eliminated

Desulfurization (TGA)

- 100 kPa pressure - 700-1000°C (scan range to find kinetic limitations), 15% CO_2, 1000 ppm SO_2 (check carbonate stability)
- 1000 kPa pressure - 900-1000°C (scan range), 15% CO_2, 1000 ppm SO_2 (check carbonate stability)

Regeneration (TGA) - Two-step process

- First Step
  100 kPa pressure - 400-1000°C (scan range), 15% CO_2, 10% H_2 + CO
  1000 kPa pressure - 400-1200°C (scan range), 15% CO_2, 10% H_2 + CO
- Second Step
  100 kPa pressure - 400°C, 25% H_2S - 650°C, 8% H_2S; remainder H_2O and CO_2 (equal parts)
  1000 kPa pressure - 400°C, 25% H_2S - 800°C, 8% H_2S

Attrition (2 in. unit)

- Desulfurization conditions; 2 m/s velocity maximum losses <0.05% of bed per hour

TABLE A3. $CaAl_2O_4$ TEST CONDITIONS

Particle size - <2000 μm; fines less than 100 μm eliminated

Desulfurization (TGA)

- 100 kPa pressure - 700-970°C (scan range), 15% CO_2, 1000 ppm SO_2
- 1000 kPa pressure - 900-1000°C (scan range)

Regeneration (TGA) - Reductive decomposition

- 100 kPa pressure - 800°C, 4% SO_2 - 1000°C, 10% SO_2; 15% CO_2, 5% H_2 + CO
- 1000 kPa pressure - 900°C, 5% SO_2 - 1000°C, 10% SO_2; 15% CO_2, 5% H_2 + CO

Regeneration* (TGA) - Two-step process

- First Step - 1000 kPa pressure, 400-690°C (scan), 15% CO_2, 10% H_2 + CO
- Second Step - 1000 kPa pressure, 300-650°C, 25% - 8% H_2S, equal parts steam and CO_2

Attrition (2 in. unit)

Desulfurization conditions; 2 m/s velocity maximum losses <1% of bed per hour

*Second regeneration scheme is examined only if the reductive decomposition scheme does not satisfy acceptance criteria.

TABLE A4. $BaTiO_3$ TEST CONDITIONS

Particle size - <2000 μm fines less than 1000 μm eliminated

Desulfurization (TGA)

- 100 kPa pressure - 700-1000°C (scan range), 15% CO_2, 1000 ppm SO_2
- 1000 kPa pressure - 900-1000°C (scan range)

Regeneration (TGA) - Reductive decomposition

- 100 kPa pressure - 800°C, 4% SO_2 - 1000°C, 10% SO_2; 15% CO_2, 5% H_2 + CO
- 1000 kPa pressure - 900°C, 5% SO_2 - 1000°C, 10% SO_2

Regeneration* (TGA) - Two-step process

- First Step - 1000 kPa pressure; 400-660°C (scan range), 15% CO_2, 10% H_2 + CO
- Second Step - 1000 kPa pressure; 300-1000°C, 25% - 10% H_2S, remainder steam

Attrition (2 in. unit)

Desulfurization conditions; 2 m/s velocity maximum losses <0.06% of bed per hour.

*The second regeneration scheme is examined only if the reductive decomposition scheme does not satisfy acceptance criteria.

APPENDIX B

ENGINEERING ASSESSMENT OF INTIMATE COAL/SORBENT MIXTURES FOR SO_2 CONTROL IN FLUIDIZED-BED COMBUSTION APPLICATIONS

PURPOSE AND SCOPE OF STUDY

This study has been carried out to investigate the technical and environmental feasibility and economic potential of "intimate coal/sorbent mixtures" when used in a fluidized-bed combustion system for power generation. Various classes of intimate coal/sorbent mixtures were first qualitatively screened for feasibility on the basis of their probable performance assessment. Intimate coal/sorbent mixtures selected as potentially feasible in the initial screening were then subjected to an engineering assessment of technical and environmental performance. Areas such as SO_x and NO_x control, trace metal and particulate control, solid waste and plant efficiency, and design factors for the fluidized-bed combustor were considered.[B1] Because no actual performance or kinetic data exist for the intimate coal/sorbent mixtures, only potential performance could be addressed and problem areas identified.

Economic potential was examined by using optimistic performance assumptions for the intimate coal/sorbent mixture. Process alternatives for the preparation of the mixtures were identified and cost projections for the preparation systems were generated.

BASIS FOR THE STUDY

The study specifically considers coal-fired fluidized-bed combustion power plants (atmospheric-pressure boilers or pressurized boilers) with once-through sorbent sulfur-removal systems. Limestones or dolomites, which are presently utilized as sulfur sorbents in these systems, are considered for the sorbent materials in the intimate coal/sorbent mixtures. Performance and economics of the intimate coal/sorbent mixture system are compared to the conventional once-through system in order to evaluate potential.

Projections for the sorbent utilization performance in a conventional fluidized-bed combustor with once-through sorbent are summarized in Table B1. Cost and environmental control projections for conventional fluid-bed combustion systems have been presented in the literature.[B2] For this study the potential range of sorbent utilizations expected in a conventional fluid-bed combustor is taken to be 50 to 90 percent for dolomites and 35 to 60 percent for limestones.

INITIAL SCREENING OF CONCEPTS

An "intimate coal/sorbent mixture" may be defined as a mixture of coal and sorbent in which the coal and sorbent are in intimate contact during the combustion and desulfurization occurring in the fluid-bed combustor. In the conventional once-through system, individual particles (-3 mesh) of coal combust within a fluidized-bed of sorbent particles (-3 mesh). Desulfurization does not appear to be kinetically controlled but is hindered by diffusion and convection of SO_2 from the burning coal particle to the sorbent particle and diffusion within the pores of the partially reacted sorbent particle. In an intimate coal/sorbent mixture these resistances might be substantially reduced, resulting in a higher utilization of the sorbent material and/or lower SO_2 emissions from the combustor.

Alternative Intimate Coal/Sorbent Mixtures

A number of general classes of intimate coal/sorbent mixtures can be conceived:

(1) Individual fine particles
(2) Consolidated particles
(3) Impregnated particles
(4) Continuous phase sorbent material or combustible material.

TABLE B1. PROJECTIONS OF THE CALCIUM-TO-SULFUR FEED RATIOS IN FLUIDIZED-BED BOILERS WITH CONVENTIONAL ONCE-THROUGH SORBENTS[a]

Sorbent	Pressure, 100 kPa		Pressurized, 1000 kPa	
	816°C	954°C	816°C	954°C
Limestone				
Uncalcined	—	—	—	—
Calcined	2.8/1	>5/1	2.2/1	2/1
Dolomite				
Half-calcined	—	—	1.6/1	1.6/1
Calcined	2.2/1	~4/1	1.2/1	1.2/1

[a] Mean particle size of 500 μm,
gas residence time = 1 second
>80% sulfur removal efficiency
from reference B2.

The first class, "individual fine particles," could consist of a fluidized-bed of very fine sorbent particles (~40 μm) in which the coal (-3 mesh) is combusted, or very fine coal particles combusted in a bed of sorbent (-3 mesh), or a bed of very fine sorbent and coal particles undergoing combustion and desulfurization, possibly in the presence of large particles. While this class might result in high combustion and/or desulfurization rates and may be potentially attractive in one of its forms, the design and operation of the fluid-bed combustor might require major modification in order to develop an economical system. In any case, this first class does not completely comply with the definition of an intimate coal/sorbent mixture in that a definite gas-phase resistance between the sorbent and coal particles will exist. This class has not been considered further in this study.

"Consolidated particles" may consist of fine sorbent particles and fine coal particles uniformly mixed and bound together into pellets, balls, or granules of about -3 mesh. Consolidated particles of this type have been produced in the laboratory.[B3,B4] The fine sorbent and coal particles might also be arranged into pellets, balls, or granules having the sorbent on the outside and the coal centralized, or in the opposite arrangement with the sorbent in the center. Similar particles have been produced in the iron ore industry.[B12] Alternating layers of fine sorbent particles could be bound to the surface of an individual or small group of coal particles to form an intimate mixture.

The third general class of mixtures, "impregnated particles," could consist of coal particles (-3 mesh) impregnated with sorbent (i.e., absorbed into the pores of the coal) or sorbent particles (-3 mesh) impregnated with coal. This is a technique applied frequently with catalyst production. Intimate contact between sorbent and coal would result.

The last class of mixtures, a "continuous sorbent phase" or a "continuous combustible phase," might consist of a slurry of coal in a

$Ca(OH)_2$ solution,[B5] or a slurry of sorbent particles in a coal/oil suspension. Under the high-temperature conditions of the combustor, the initially continuous phase would not remain so. The $Ca(OH)_2$ solution would be immediately transformed into a very fine precipitate of CaO which would react quickly with SO_2 to form a fine calcium sulfate precipitate. The coal/oil suspension would crack thermally and combust, as in the fluidized-bed combustion of liquid fuels. This class would ultimately behave similarly to the first class of individual fine particles.

From the four classes of intimate coal/sorbent mixtures, only the consolidated particles class was considered further. The ability of coal to become impregnated with sorbent or sorbent to become impregnated with coal to the extent required (about 10 to 30 weight percent sorbent in coal) appears very doubtful. The slurry of coal in a $Ca(OH)_2$ solution would result in the entrainment of a large amount of extremely fine (∿5 μm or less) particles from the bed. Also involved would be a great quantity water and an associated reduction in plant thermal efficiency due to the evaporation of this water. Only the consolidated particle concept appears to be feasible and to merit further assessment.

Alternative Coal/Sorbent Consolidated Particle Characteristics

A coal/sorbent consolidated particle may exhibit many characteristics which will greatly influence the performance of the fluidized-bed combustor and will determine the type of equipment required to prepare the particles. Table B2 summarizes the consolidated particle characteristics, their ranges of values, and the influences which they have on the plant performance and design.

If the relationships between the consolidated particle characteristics and the factors they influence were known, the optimum characteristics and the preparation equipment that would provide them could be selected. Without this information a qualitative judgement is required to assess these factors.

Alternative Coal/Sorbent Consolidated Particle Preparation System

A general schematic process flow diagram for the consolidated particle preparation system is shown in Figure B1. The preparation system will in general consist of handling equipment for coal and sorbent, crushing and pulverizing equipment for coal and sorbent, mixing equipment for the coal and sorbent, size enlargement equipment to form the consolidated particles, and equipment to feed the consolidated particles to the fluidized-bed combustor.

A number of options exist for the separate stages of the preparation system, many of which are related to the consolidated particle characteristics discussed in Table B2. Some of these options are addressed in Table B3. In addition to these options, if coal is pulverized to a very fine size, a mechanical cleaning process might be utilized to remove considerable ash, trace elements, and pyritic sulfur following the pulverization.[B6,B7] An absorbent for trace element control might also be incorporated into the consolidated particles. These additional options have not been considered further in this study.

PROJECTIONS OF ENVIRONMENTAL AND TECHNICAL PERFORMANCE

Factors that are of concern to the environmental and technical performance of the fluidized-bed combustor are technical factors such as the combustion efficiency, heat transfer rates, bed mixing, or bed temperature uniformity; and environmental factors such as SO_x control, NO_x control, trace element release, particulate control, solid waste, sorbent utilization, and so on. Without carrying out detailed modeling or experimental investigation of the behavior of coal/sorbent consolidated particles, it is impossible to evaluate these factors. It is possible to speculate, however, about the possible behavior of the consolidated particles in a fluidized-bed combustion system.

In order for a fluidized-bed combustion power plant to be economical, the fluidization velocity in the combustor must be in the range of

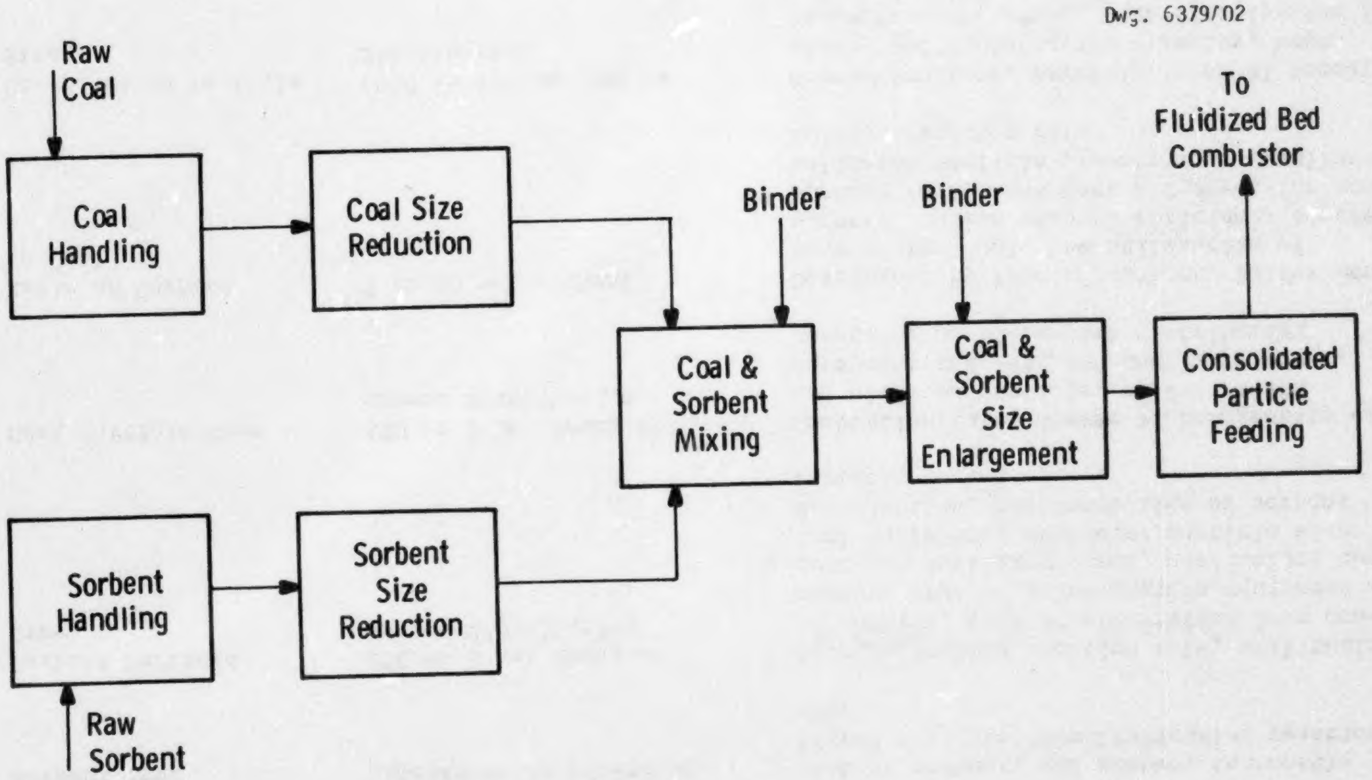
Dwg. 6379/02
Raw Coal
Coal Handling
Coal Size Reduction
Binder
Binder
To Fluidized Bed Combustor
Coal & Sorbent Mixing
Coal & Sorbent Size Enlargement
Consolidated Particle Feeding
Sorbent Handling
Sorbent Size Reduction
Raw Sorbent

Figure B1. Coal/sorbent consolidated particle preparation system

TABLE B2. COAL/SORBENT CONSOLIDATED PARTICLE CHARACTERISTICS

CHARACTERISTIC	RANGE	INFLUENCES
Sorbent Type	Limestones or dolomites	Cost of sorbent, wt% sorbent in consolidated particle, desulfurization reaction rate
Sorbent Particle Size	250 to 2 μm; broad or narrow distribution	Desulfurization reaction rate, utilization of sorbent, rate of elutriation from combustor, type of pulverization equipment and cost and auxiliary power, particulate control equipment, combustor particle size distribution, residence time of sorbent particle in bed
Coal Particle Size	500 to 2 μm; broad or narrow distribution	Combustion rate, degree of homogeneity of consolidated particle, pulverization equipment and cost, and auxiliary power, combustor particle size distribution
Ratio of Sorbent to Coal	5 to 50 wt% sorbent	Determined by type of sorbent, sulfur content of the coal, the utilization of sorbent, sulfur removal efficiency of combustor; influences cost and power for consolidated particle preparation, desulfurization reaction rate
Consolidated Particle Size	6000 to 100 μm; narrow distribution	Combustion rate, particle internal temperature, bed fluidization velocity, heat transfer coefficient, size distribution in bed, bed residence time of sorbent, bed mixing uniformity, type of preparation equipment

TABLE B2 (Continued)

CHARACTERISTIC	RANGE	INFLUENCES
Consolidated Particle Shape	Cylindrical, spherical, irregular	Type of size enlargement equipment, fluidization velocity, heat transfer, bed mixing, general fluidization properties
Consolidated Particle Compaction	Loose to compact	Reaction rates, particle strength and density, bed-size distribution, preparation equipment
Distribution of Coal and Sorbent in the Consolidated Particle	Sorbent on surface, coal on surface, uniformly mixed, in multiple layers	Combustion and desulfurization rates, utilization of sorbent, residence time of sorbent in bed, strength of particle, type of size enlargement equipment
Binder Type and Amount[B11-B15]	Pitch, asphaltum, oil, lime sodium silicate, cellulose, bentonite (clay), water; 2 to 50 wt% binder or pressure only (as in briquetting)[B14]	Strength of particle, attrition rate and elutriation rate, bed particle-size distribution, emissions from combustor, operating cost of plant

TABLE B3. CONSOLIDATED PARTICLE PREPARATION SYSTEM OPTIONS

Coal and Sorbent Handling - Conventional equipment

Coal and Sorbent Size Reduction -

Type of equipment: crushers and grinding mills (slow speed, medium speed, high speed and fluid-jet pulverizer catagories); equipment type depends on size reduction required.[B8-B11]

Degree of crushing size-reduction compared to grinding size-reduction: an optimum exists in terms of power and cost for the extent of crushing followed by grinding to produce a given particle size.

Coal and Sorbent Mixing -

Type of equipment: tumblers, stationary shell, shell and internal device rotate, impact mixers
Continuous or batch[B11]

Coal and Sorbent Size Enlargement -

Type of equipment: compaction (as pellet mill or briquetting equipment, tumbling (as disk or drum), briquetting followed by curshing, pressing followed by granulation; depends upon characteristics of the product required[B11-B14]

Consolidated Particle Feeding -

The strength of the particles and their flowability may affect the equipment design about 0.6 to 3.0 m/sec. In any case, the fluidization velocity will certainly be greater than the terminal velocities of the individual coal and sorbent particles composing the consolidated particles.

Because of this practical constraint, it appears that the consolidated particle attrition behavior (before, during, and following combustion) is the single most critical consolidated particle property relating to the performance of the fluidized-bed combustor. The type of binder material may also then be a critical factor. The consolidated particle attrition behavior for a given fluidization velocity will determine three important characteristics of the fluidized bed — the particle size distribution in the bed, the residence times of coal and sorbent particles in the bed, and the nature of fluidization in the bed. These characteristics will in turn determine the load on the particulate control equipment and the fines recycle rate, the heat transfer rates and temperature gradient in the combustor, the extent of SO_x control and the utilization of the sorbent, the particulate emissions from the plant, and the nature of the solid waste. They may also relate to trace element release and NO_x control.

Table B4 summarizes the speculative performance of coal/sorbent consolidated particles. The overall performance to be expected is very uncertain.

Some evidence does exist, though limited, that the basic sulfur removal process will function in the consolidated particles (i.e., the ability of high-calcium content lignite to burn with reduced sulfur release,[B16] and the ability of laboratory-fabricated consolidated particles to desulfurize in a conventional pulverized-coal boiler).[B4]

ECONOMIC PROJECTION

The economics of the coal/sorbent consolidated particle concept are estimated on the basis of a set of very optimistic performance assumptions in order to identify the maximum economic potential for the concept. The major assumption applied is that 100 percent utilization of the sorbent particles (limestone or dolomite) can be realized, and all other performance aspects are acceptable. It is also assumed that the cost of coal and sorbent handling equipment, coal/sorbent consolidated particle feeding equipment, and all other plant equipment other than the consolidated particle preparation system are identical in cost to the conventional fluidized-bed combustion plant (i.e., the combustor, solids feeding system, and particulate removal equipment are identical in cost to the conventional plant). Thus, only the cost of the consolidated particle preparation system is considered.

A 600 MWe power plant is selected for the estimates, and a plant heat rate of 9.5 MJ/kWh is assumed (excluding power requirements for the consolidated particle preparation).

Economic Incentive

The potential economic advantage or disadvantage of the consolidated particle concept is demonstrated by comparing the operating-cost savings obtained by the assumed reduction in the rate of sorbent consumption (due to assumed 100 percent utilization) with the increased operating cost associated with capitalization on the preparation system capital investment. Comparison may also be made with the cost of auxiliary power (or loss of plant efficiency) needed for consolidated particle preparation.

A number of parameters are involved: the weight fraction of sulfur in the coal (and the binder material), the heating value of the coal (and the binder material), the type of sorbent (limestone or dolomite), the utilization of the sorbent in the conventional fluid-bed combustor, and the cost of the sorbent.

The required sulfur removal efficiency, ε_s, for a given coal (assuming no binder sulfur or binder sulfur or binder heating value) is

$$1 - \varepsilon_s = \frac{SH}{\omega_s \, 2 \times 10^6} \qquad (1)$$

where S is the environmental standard for sulfur emission from the plant, ($kgSO_2/GJ$), H is the coal-heating value of the coal (MJ/kg), and ω_s is the weight fraction of sulfur in the coal. The Federal EPA emission standard, S, is currently 0.516 $kgSO_2/GJ$ for large, conventional coal-fired boilers, H may range from 23.2 MJ/Kg up to 35.0 MJ/kg for eastern coals, and ω_s may range from 0.01 up to 0.06. Figure B2 shows the required sulfur removal efficiency as a function of the parameters in Equation (1).

For a once-through sorbent, the consumption rate of sorbent is given by

$$M = \varepsilon_s/\overline{U} \quad , \tag{2}$$

where M is the sorbent feed rate in moles calcium per mole of sulfur in the coal, and $\overline{U}$ is the average utilization (fraction of the calcium reacted) of the sorbent in the combustor. For the coal/sorbent consolidated particle it is assumed that $\overline{U} = 1.0$ and thus

$$M = \varepsilon_s \quad . \tag{3}$$

Figure B3 relates the maximum difference between the sorbent feed rates in the conventional fluidized-bed combustion and consolidated particle cases as a function of the conventional sorbent utilization and coal sulfur content.

The operating cost savings due to the assumed reduced sorbent feed rate with the consolidated particle concept is expressed in Figure B4 in mills/kWh. The figure assumes a dolomite sorbent with a molecular weight of 184, a sorbent purchase and disposal cost of $11/Mg and a coal-heating value of 23.2 MJ/kg . For a limestone sorbent having a molecular weight of 100, the cost savings in Figure B4 would be divided by 1.84. A coal-heating value of 35 MJ/kg for a coal sulfur content ω_s would be equivalent to the cost savings for a 23.2 MJ/kg heating value coal having a sulfur content of $\omega_s/1.5$. The cost savings is directly proportional to the purchase and disposal cost of the sorbent material (the disposal cost is assumed identical for the conventional and consolidated particle cases).

TABLE B4. SPECULATIVE PERFORMANCE OF COAL/SORBENT CONSOLIDATED PARTICLES

Consolidated Particle Attrition -

- Attrition can occur because of mechanical forces (feeding, bed-mixing distributor air jets) or because of decrepitation during combustion of the particles.
- Some softening of the coal during heat-up may initially strengthen the consolidated particles.
- During combustion ash and sorbent particles will probably continuously break off as combustion proceeds inward. Ash from the binder material may also break off. Complete reduction of the consolidated particle to fine ash (coal and binder) and individual sorbent particles is expected, with all of this material being elutriated from the combustor unless a binder is identified that would retain the structural integrity of the consolidated particle even following combustion.

Combustion -

- The consolidated particles may be more porous than single coal particles and may combust more rapidly and more uniformly.

to

- If mechanical attrition of the consolidated particles occurs to anv extent, coal particle elutriation (carbon carry-over) could result in lower combustion efficiency.
- The consolidated particle temperature will be greater than the bulk bed temperature (possibly by several hundred degrees centigrade) during combustion.

General Fluidization Behavior -

- The average particle size in the combustor will probably have a terminal velocity less than the superficial fluidization velocity, resulting in a high cyclone-fines recirculation rate requirement.
- The bed will probably be a fast or elutriated fluidized-bed with heat transfer and bed mixing much different from a bubbling fluidized bed.

TABLE B4 (Continued)

Binder Behavior -

- Ideally, a binder would provide resistance to mechanical attrition and decrepitation due to combustion, resulting in a combusted particle that maintains physical strength and contains the coal ash and utilized sorbent in a single mass. It appears that none of the binders listed in Table B2 will display this property.
- Water as a binder would quickly evaporate and lead to break-up of the consolidated particle unless coal softening provides sufficient liquid bridges to maintain the particle strength.
- Other proposed binders will probably combust or decompose during the combustion of the consolidated particle.

SO_2 Absorption and Sorbent Utilization -

- The sorbent particles should be of a size (probably <40 μm) that would be expected to react quickly (∿2 min) with SO_2 to a very high level of utilization.
- The sorbent residence time in the combustor depends upon the consolidated particle combustion rate, attrition rate, and the rate of elutriation of the sorbent particles from the bed.
- Desulfurization will occur while the sorbent particles are situated within the consolidated particle and also following attrition when the sorbent particle is exposed to the bulk combustor gas.
- The sorbent particles with the consolidated particle should be exposed to higher SO_2 concentrations than is the sorbent in a conventional fluid-bed combustor due to decreased dilution. Higher reaction rates should result.
- On the other hand, high CO_2 concentrations in the consolidated particle may limit calcination of the sorbent and reduce sulfur reactivity.
- Because of the possible high consolidation particle temperature during combustion, the equilibrium SO_2 driving force will be reduced relative to its value at the bulk bed temperature. Also, the sorbent particles may quickly sinter, leading to deactivation and limited utilization.

TABLE B4 (Continued)

NO_x Control -

- NO_x formation appears to be more sensitive to the combustion conditions (excess air, bed temperature) and possibly the sulfur level in the gas than it is to the distribution of coal and sorbent. While the mechanism of NO_x formation is not well understood, it is not felt that the coal/sorbent consolidated particle concept would significantly influence NO_x emission from the combustor.

Trace Element Release -

- Because the sorbent particles are exposed to a higher temperature than in a conventional fluid-bed combustor, the release of trace elements from the sorbent may increase.

- The binder material may also release trace elements.

- The trace elements released from the coal, sorbent, and binder may have an opportunity to react with an absorbent incorporated into the consolidated particle. Coal ash also may act as a trace element getter. A binder such as bentonite (contains kaolinite and montmorillonite) may also function as a getter.

- Washing the pulverized coal during consolidation particle preparation may eliminate some trace element content.

Particulates -

- The use of consolidated coal/sorbent particles will probably place a greater demand on the particulate control equipment and may result in high particulate emissions from the plant. Turbine protection from the erosion standpoint will be more difficult in the case of the pressurized system.

- On the other hand, identification of an indestructible binder could improve the particulate control situation.

Solid Waste -

- Coal-ash quantity will probably be identical to a conventional fluidized-bed combustion power plant.

TABLE B4 (Continued)

- Spent sorbent waste quantity may be reduced if an improvement in sorbent utilization can be realized, but the waste fines may be more difficult to handle than the coarse waste from a conventional fluidized-bed combustion power plant.
- Additional waste from the binder material will also exist.
- Leaching properties of the solid waste may also be modified as a result of the binder.

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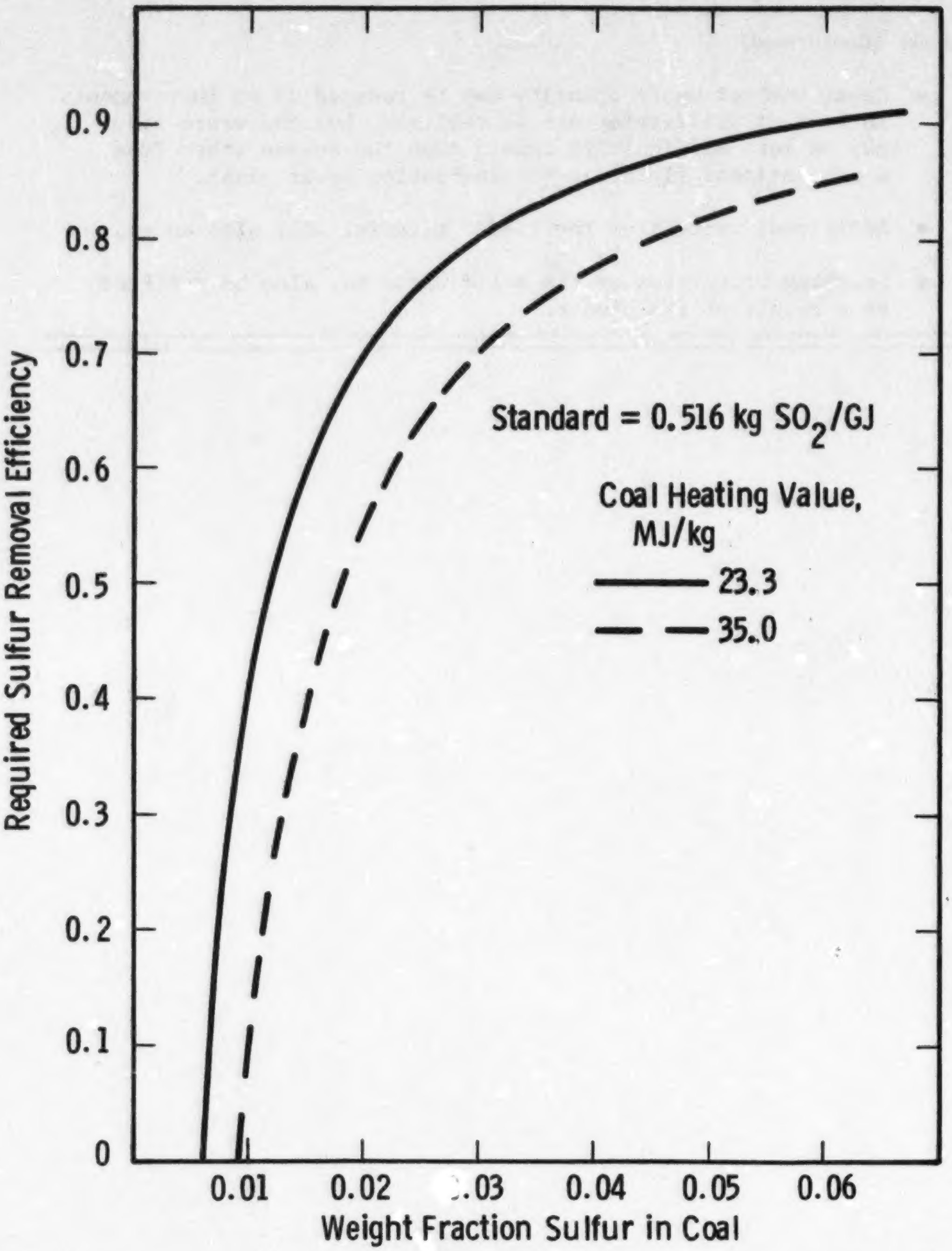


Figure B2 — Combustor sulfur removal efficiency required to achieve U. S. EPA emission standard

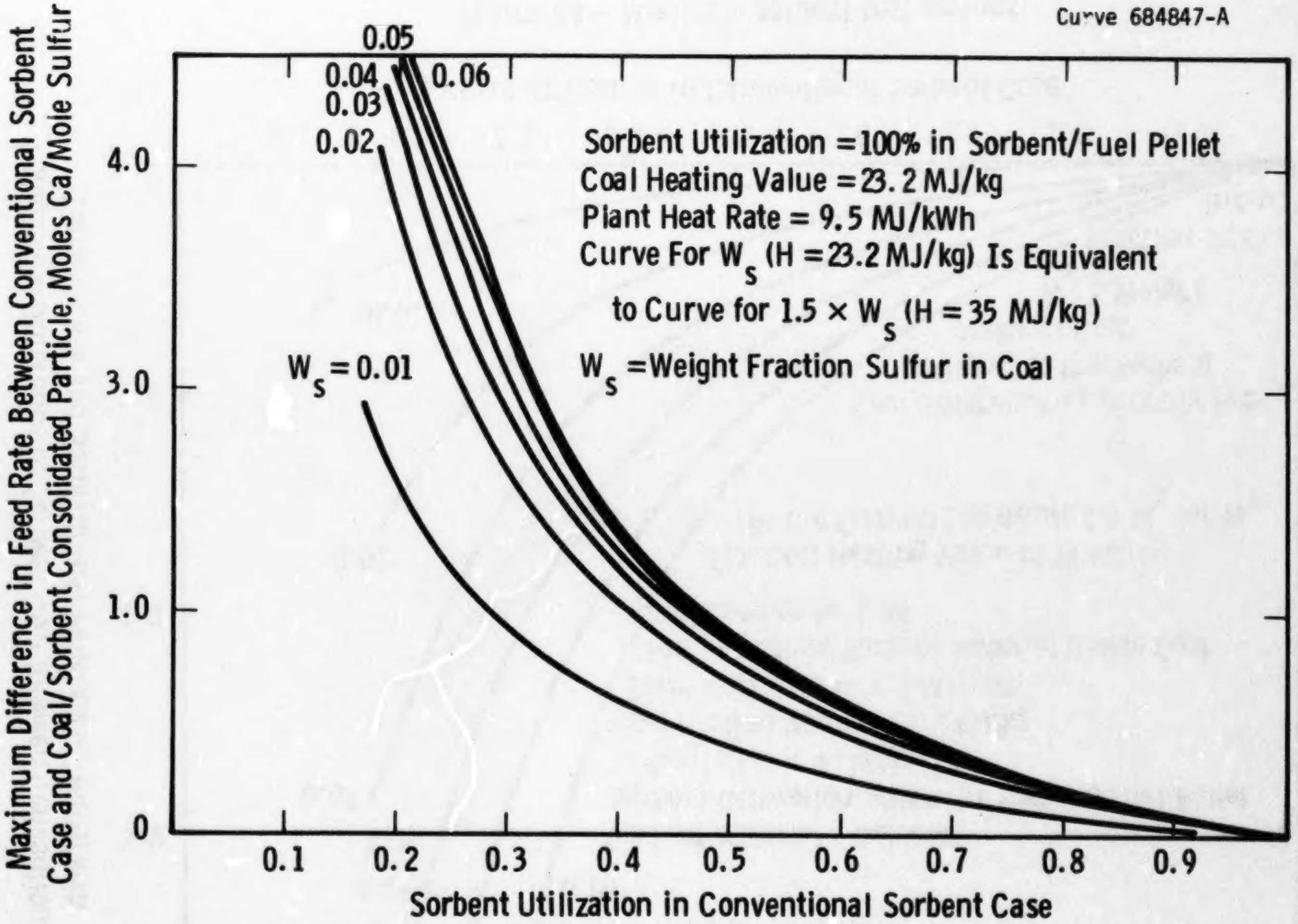


Figure B3 — Maximum difference in sorbent feed rates

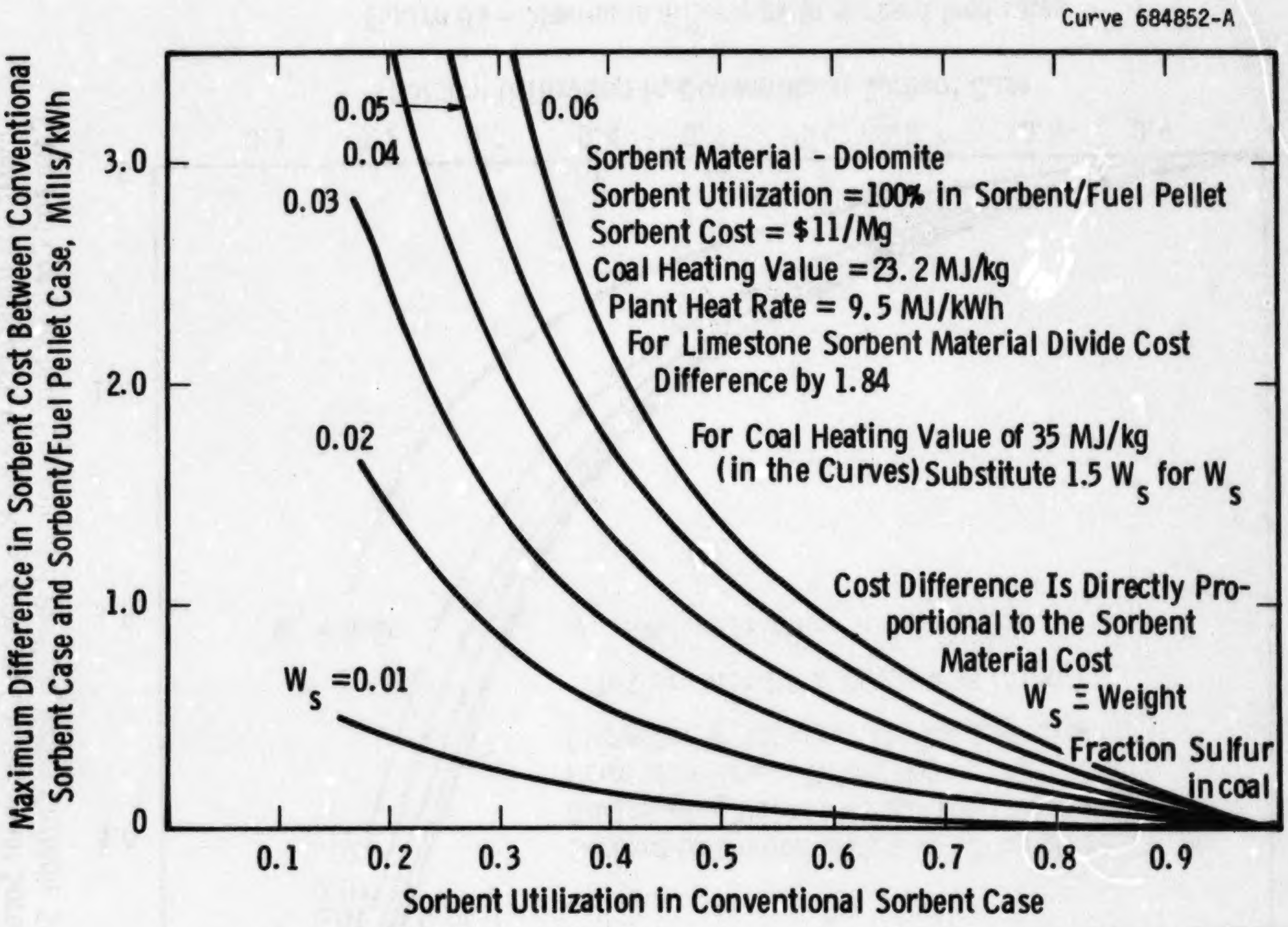


Figure B4 — Maximum sorbent cost savings

Maximum Acceptable Costs for Consolidated Particle Preparation

The power plant total energy cost resulting from the consolidated particle preparation system consists of contributions from fixed charges on the capital investment, operating and maintenance costs, auxiliary power costs, and the cost of auxiliary fuel and chemicals (binder, etc.). Neglecting all items except the capital charges permits the calculation of a maximum break-even capital investment for the preparation system equipment, where fixed charges for the capital investment equal the maximum savings shown in Figure B4 for the consolidated particle system. The maximum break-even capital investment is shown in Figure B5 for a dolomite sorbent costing \$11/Mg, a coal-heating value of 23.2 MJ/kg, a capacity factor of 70 percent and a capitalization of 15 percent/yr. The maximum break-even investment is directly proportional to the sorbent purchase and disposal cost.

In a similar manner a maximum break-even auxiliary power requirement for the preparation system may be determined (assuming no capital charges, operating and maintenance cost, or auxiliary fuel and chemicals). In this case the auxiliary power is treated as a reduction in the power plant heat rate. This calculation is represented in Figure B6 as a percentage of the power plant output for a dolomite sorbent, a sorbent cost of \$11/Mg, and a total power plant energy cost without consolidated particle preparation of 19.0 mills/kWh (based on a pressurized combustion system with a plant heat rate of 9.5 MJ/kWh.[B2]

The actual break-even capital investment and break-even power requirement will be less than the maximum break-even values given in Figures B5 and B6 if all factors are simultaneously considered. In some cases binder material may be expensive and maintenance costs very high.

Consolidated Particle Preparation System Cost Estimate

For the purposes of providing a cost estimate for the consolidated particle preparation system, the following basis has been selected:

- 600 MWe plant
- Coal rate of 227 Mg/hr

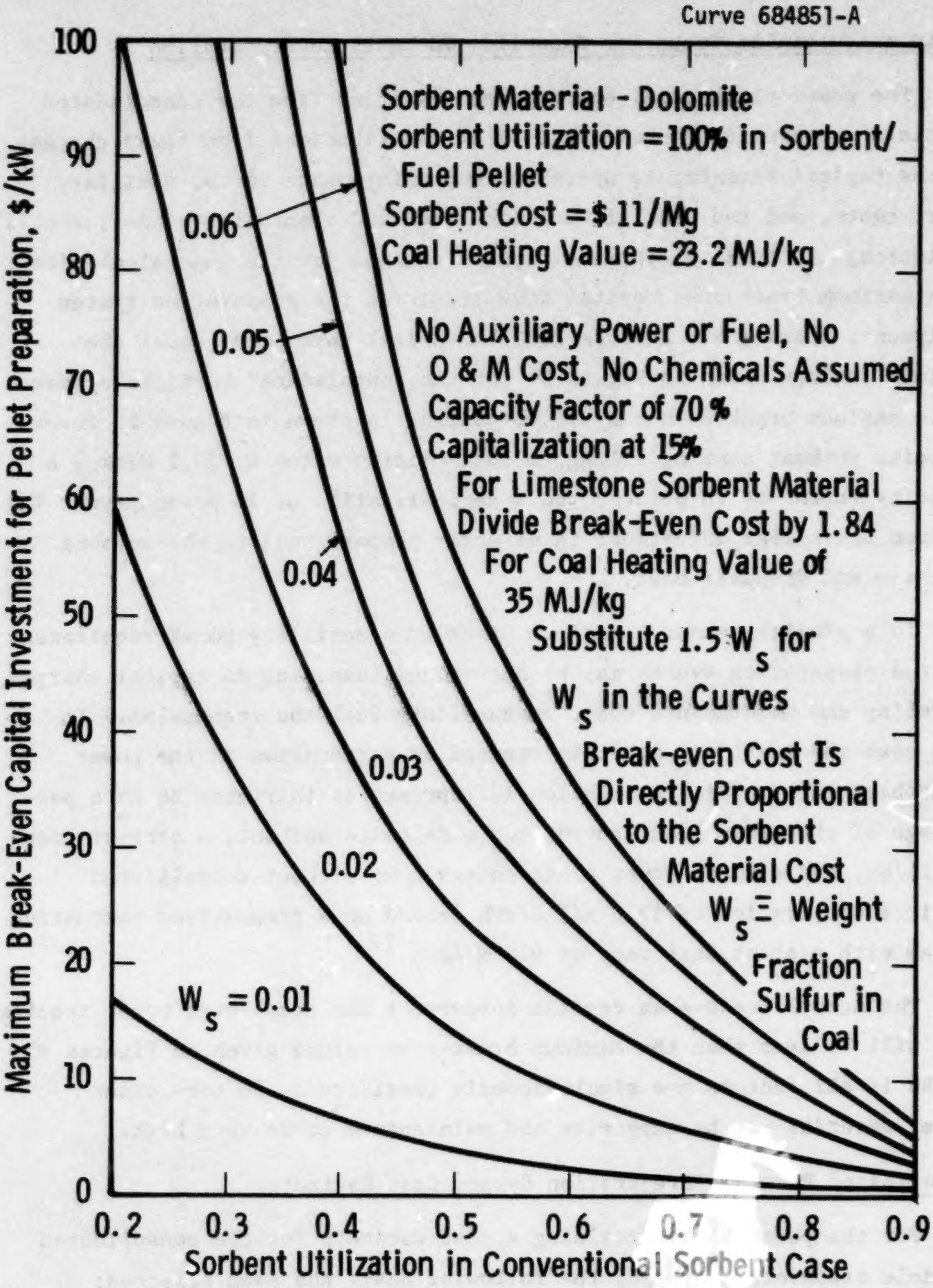


Figure B5 — Maximum break-even capital investment

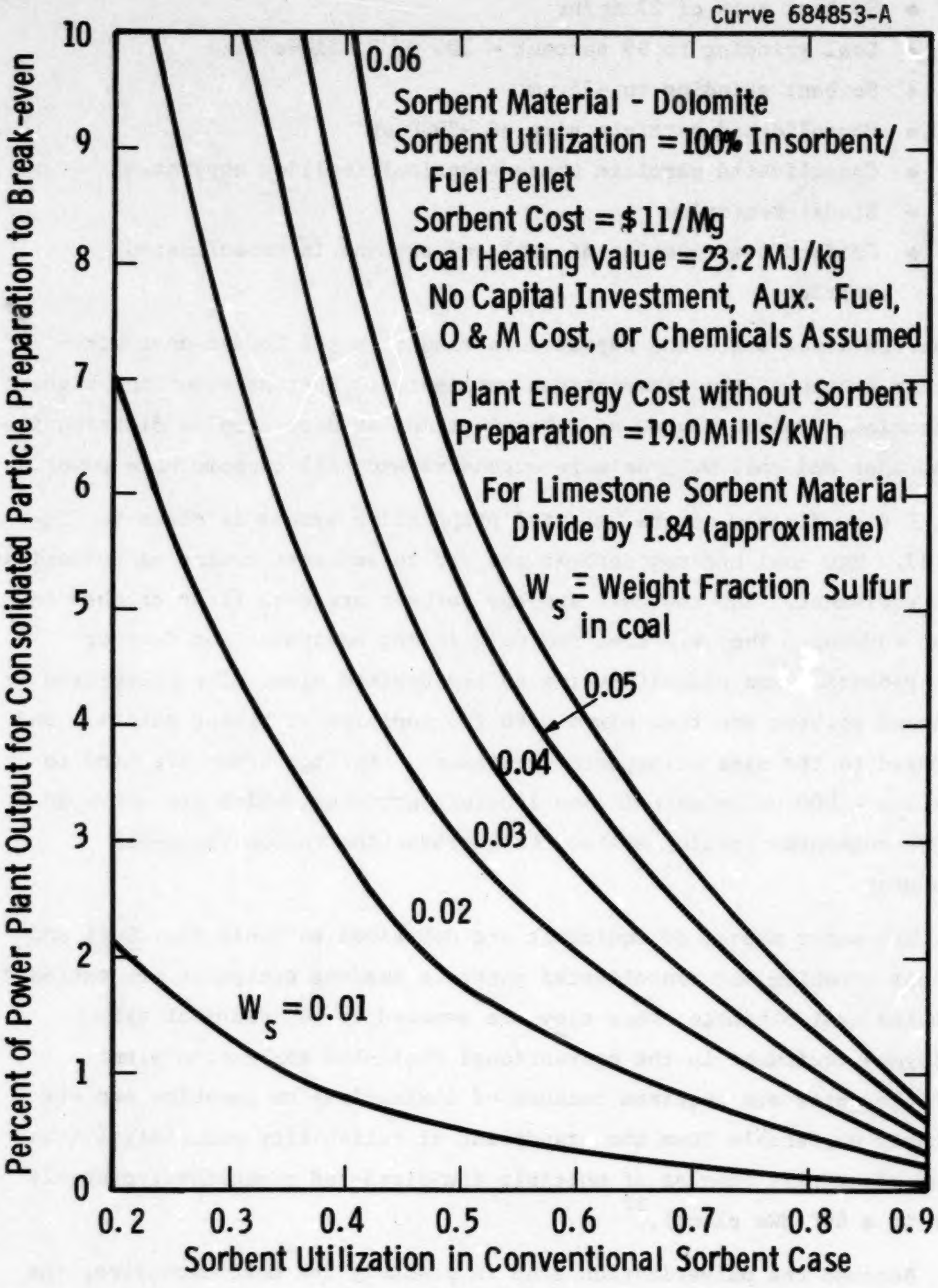


Figure B6 — Break-even power requirement

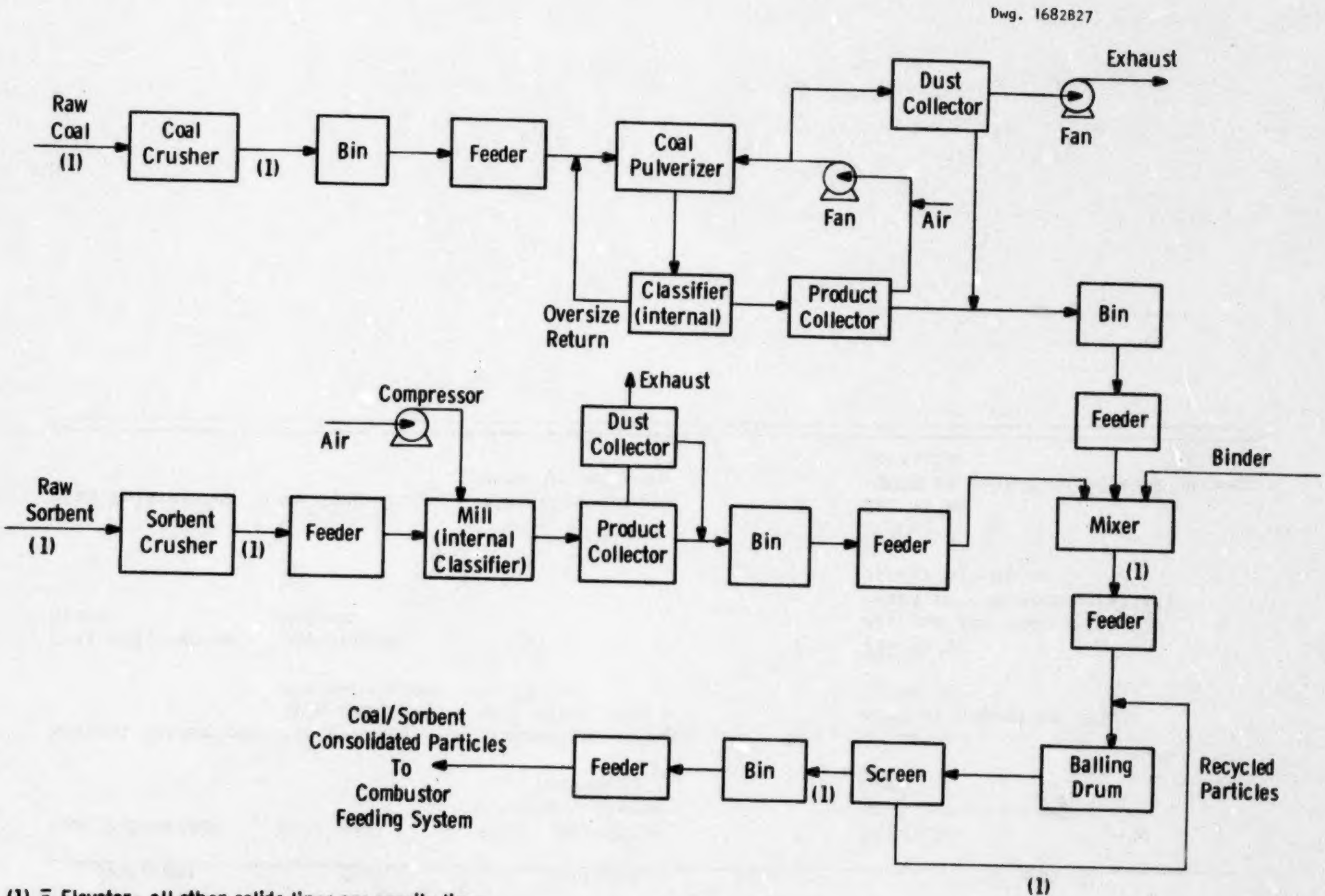
- Sorbent rate of 27 Mg/hr
- Coal grinding to 99 percent - 200 U. S. Sieve Size
- Sorbent grinding to -25 μm
- Consolidated particle size of -3000 μm
- Consolidated particle shape spherical (balling apparatus)
- Binder-bentonite
- Uniform distribution of coal and sorbent in consolidated particle.

These characteristics are expected to result in the lowest-cost preparation system of the alternatives considered. Systems requiring higher compaction, greater degree of pulverization, or more complex distribution of sorbent and coal will be more expensive and will consume more power.

A flow diagram of the selected preparation system is shown in Figure B7. Raw coal and raw sorbent are fed to separate trains of pulverization equipment. The raw coal and raw sorbent are each first crushed to about -300 μm. They are then fed to grinding equipment for further size reduction and classification to the desired size. The pulverized coal and sorbent are then mixed with the addition of binder material and conveyed to the size enlargement equipment. Balling drums are used to generate -3000 μm spherical consolidated particles, which are conveyed to the combustor feeding system for introduction to the fluid-bed combustor.

The major pieces of equipment are described in Table B5. Coal and sorbent crushing and consolidated particle feeding equipment are excluded from the cost estimate since they are assumed to be identical with analogous equipment in the conventional fluid-bed combustion plant. Multiple units are required because of limitations on capacity and are probably preferable from the standpoint of reliability and control (the power plant will consist of multiple fluidized-bed combustors; probably four in a 600 MWe plant).[B2]

Because the pulverization step is probably the most expensive, the most power-consuming, and the highest-maintenance operation in the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Raw Coal (1)
Coal Crusher
(1)
Bin
Feeder
Coal Pulverizer
Dust Collector
Exhaust
Fan
Fan
Air
Classifier (internal)
Oversize Return
Product Collector
Bin
Feeder
Binder
Compressor
Air
Raw Sorbent (1)
Sorbent Crusher
(1)
Feeder
Mill (internal Classifier)
Exhaust
Dust Collector
Product Collector
Bin
Feeder
Mixer
(1)
Feeder
Recycled Particles
Balling Drum
Screen
(1)
(1)
Bin
Feeder
Coal/Sorbent Consolidated Particles To Combustor Feeding System

(1) Ξ Elevator; all other solids lines are gravity lines

Figure B7. Coal/sorbent consolidated particle preparation system

TABLE B5. DESCRIPTION OF SELECTED PREPARATION EQUIPMENT

Equipment	Type	Includes	Number Required	Specification
Coal Pulverizer	Ball mill	Fans, classifier, product collector, dust collector	8	227 Mg/hr coal ground to 99% -200 mesh
Sorbent Pulverizer	Fluid energy-type such as Mikro-Atomizer	Compressor, product collector, dust collector	20	27 Mg/hr sorbent ground to -25μm diameter
Coal and Sorbent Mixer	Continuous Muller		8	254 Mg/hr sorbent and coal uniformly mixed with binder material; binder ∿25 Mg/hr
Size Enlargement	Balling drum	Vibrating screen, recycle conveyor	8	281 Mg/hr -3000 μm consolidated coal/sorbent particles

preparation system, the degree of size reduction must be carefully selected. Figure B8 shows the power required for coal pulverization for two general classes of size-reduction equipment: mechanical mill-type grinders and fluid energy-type grinders. Data have been collected from the literature and show that the power requirement rises steeply with decreased product diameter and that the fluid-energy mill uses less power for a given size reduction when the product size drops below about 40 µm.[8-11] The same behavior is seen for sorbent pulverization, shown in Figure B9.

Cost projections for pulverization systems based on projections from a few cost data points are presented in Figure B10. The cost in $/kW rises steeply as the degree of pulverization increases. The mechanical mill-type pulverizers and fluid-energy mills are about on the same line for sorbent product particle sizes greater than around 50 µm, but the fluid-energy mills cost more for the coal pulverization because of the large number required. A trade-off exists between power required and capital investment when selecting from the two general classes of grinders. It appears that pulverizing coal to less than approximately 50 µm diameter would not be economically feasible. Sorbent pulverization to -25 µm does appear feasible using fluid-energy mills, although a large number may be required (about 20 for a 27 Mg/hr rate).

A cost breakdown for the consolidated particle preparation systems is shown in Table B6. Power requirements are also indicated. A total capital investment of $42.7/kW is projected with a power requirement of 12.6 MWe (2.1 percent of plant power).

Table B7 compares the projected cost investment and power requirements for limestone and for dolomite sorbents with the maximum break-even capital investment and power requirement presented in Figures B5 and B6.

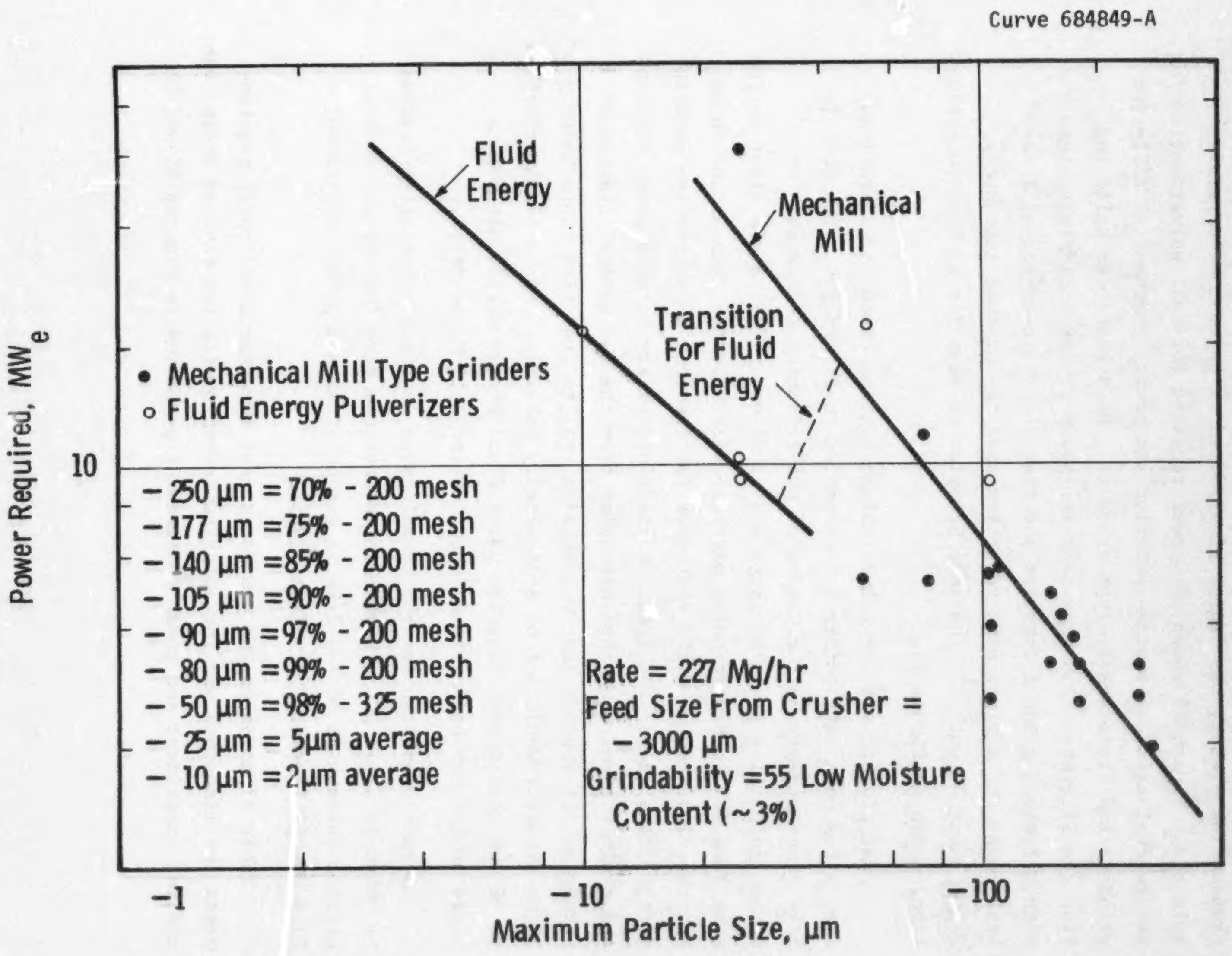

Figure B8 — Coal pulverization power requirement

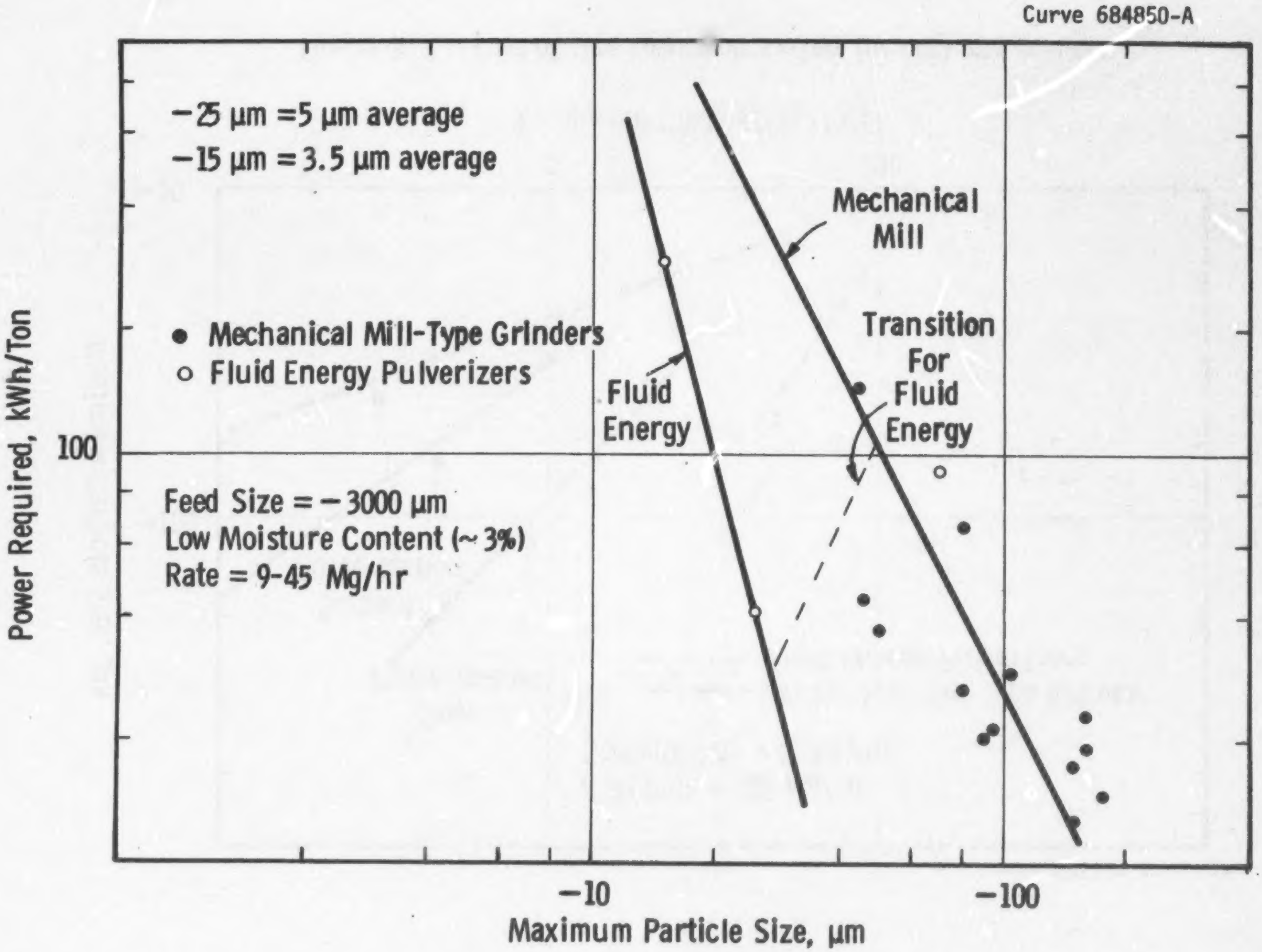

Figure B9 — Sorbent pulverization power requirement

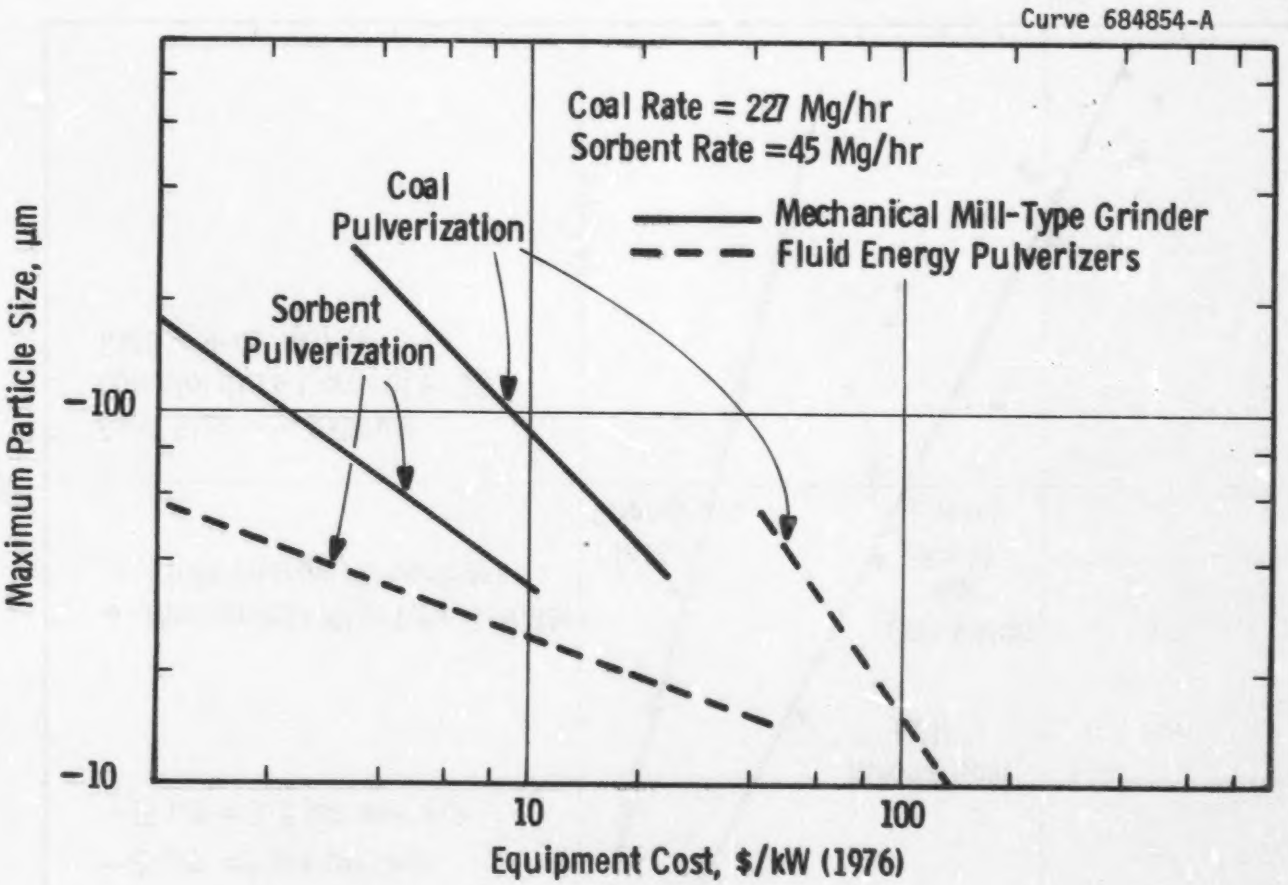

Figure B10 — Cost of size reduction system for coal and sorbent

TABLE B6. COST ESTIMATE FOR CONSOLIDATED PARTICLE PREPARATION

Installed Equipment Cost	$/kW	Power (MWe)
Coal-grinding system	11.0	8.5
Sorbent-grinding system	10.0	2.1
Coal and sorbent mixing	3.2	1.0
Size enlargement system	3.8	0.5
Bins, feeders, elevators, etc.	1.0	0.5
Total Direct Cost	29.0	12.6
Indirect Cost	7.2	
Contingency and Fee (18%)	6.5	
Total Cost	42.7	

Basis -

- 600 MWe plant
- 227 Mg/hr coal
- 27 Mg/hr sorbent
- 1976 cost basis

TABLE B7. COMPARISON BETWEEN BREAK-EVEN FACTORS AND ESTIMATES[a]

	Limestone Sorbent		Dolomite Sorbent	
Weight Percent Sulfur in Coal	Maximum Break-Even Cost ($/kW)	Cost Estimate ($/kW)	Maximum Break-Even Cost ($/kW)	Cost Estimate ($/kW)
6	20-60	38-43	6.5-55	40-48
5	16-53		5.5-45	
4	13-40		4.0-35	
3	9-27		3.0-25	
2	5-16		1.5-14	
1	1.5-5		0.5-4	
	Maximum break-even power (%)	Power estimate (%)	Maximum break-even power (%)	Power estimate (%)
6	2.3-6.5	1.9-2.1	0.8-6.2	2.1-2.5
5	2.0-5.6		0.7-5.2	
4	1.5-4.5		0.5-4.2	
3	1.1-3.0		0.4-3.0	
2	0.6-2.0		0.2-1.8	
1	0.2-0.5		0.1-0.5	

[a] Basis - see Figures B5 and B6.

- 100% utilization of the consolidated particle sorbent
- Limestone/dolomite cost - $11/Mg ($10/ton) (purchase and disposal)
- Limestone utilization ranges from 0.35 to 0.60 in conventional fluid-bed combustion
- Dolomite utilization ranges from 0.50 to 0.90 in conventional fluid-bed combustion
- The left-hand figure in the break-even columns for cost and power refers to maximum utilization of the sorbent, the right-hand figure refers to minimum utilization.
- The left-hand figures in the cost and power estimate columns refer to 1% sulfur coal and the right-hand columns refer to 6% coal.

It is evident from Table B7 that for a sorbent cost of \$11/Mg and 100 percent utilization of the consolidated particle sorbent:

- If maximum utilization of limestone or dolomite sorbents can be obtained in conventional fluidized-bed combustors (60 and 90 percent, respectively), either the capital investment or the auxiliary power requirement alone makes the consolidated particle concept appear economically not competitive.
- If only minimum utilization of limestone or dolomite sorbents can be obtained in conventional fluidized-bed combustors (35 and 50 percent, respectively), either the capital cost or the auxiliary power alone still makes the consolidated particle concept appear economically not competitive for coal-sulfur contents of less than 4 weight percent.
- If all cost factors are considered (capital charges, auxiliary power, operating and maintenance, auxiliary fuel and chemicals, coal losses, etc.) simultaneously, the consolidated particle concept will not be economically competitive with a sorbent cost of \$11/Mg, at any coal sulfur content.

The only circumstances under which the consolidated sorbent concept could be economically competitive are:

- If all the optimistic assumptions applied could be realized - 100 percent utilization of the sorbent in the consolidated particle, no additional capital investment associated with the fluid-bed combustor, particulate control equipment, feeding equipment, spent sorbent processing, etc., - and, simultaneously,
- If the sorbent material were very expensive, (>\$20/Mg), the available coal contained more than 5 weight percent sulfur and the conventional sorbent utilization performance was very poor.

ASSESSMENT

- The only technically feasible intimate coal/sorbent mixture that could be identified for the current fluidized-bed combustion design concept is the consolidated coal/sorbent particle concept.
- Attrition of the consolidated particle is the most critical factor influencing the performance and feasibility of the concept. Modifications to the combustor design would probably be required in order to apply the consolidated particle concept.
- The performance (technical and environmental) cannot be estimated without initiating a test program. The overall technical and environmental performance of the consolidated particle concept could conceivably be worse than or better than the conventional fluid-bed combustor, but it is highly unlikely that any significant improvement in performance is to be realized.
- Except under very extreme conditions, the consolidated particle concept will not be economically competitive with conventional fluid-bed combustion concepts.
- Washing the pulverized coal during consolidated particle preparation could reduce trace elements, ash, sulfur, and the sorbent requirement. The economics of this option have not been investigated.
- The most attractive consolidated coal/sorbent particle from the standpoint of technical and environmental impact would utilize a binder that would maintain the coal-ash and sorbent particles in discrete, consolidated particles following combustion. A binder that will effect this behavior has not been identified.

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